Fluorinated Electrolyte for 5-V Li-Ion Chemistry

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Argonne National Laboratory

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Project ID #: ES218

Project Overview

Timeline

- Project start date: Oct. 1, 2013
- Project end date: Sept. 30, 2015
- Percent complete: 50%

Barriers

- Low oxidation stability of electrolyte
- High, low temperature performance
- Poor cycling life due to the instability of electrode/electrolyte interface
- Safety concern associated with high flammability and reactivity

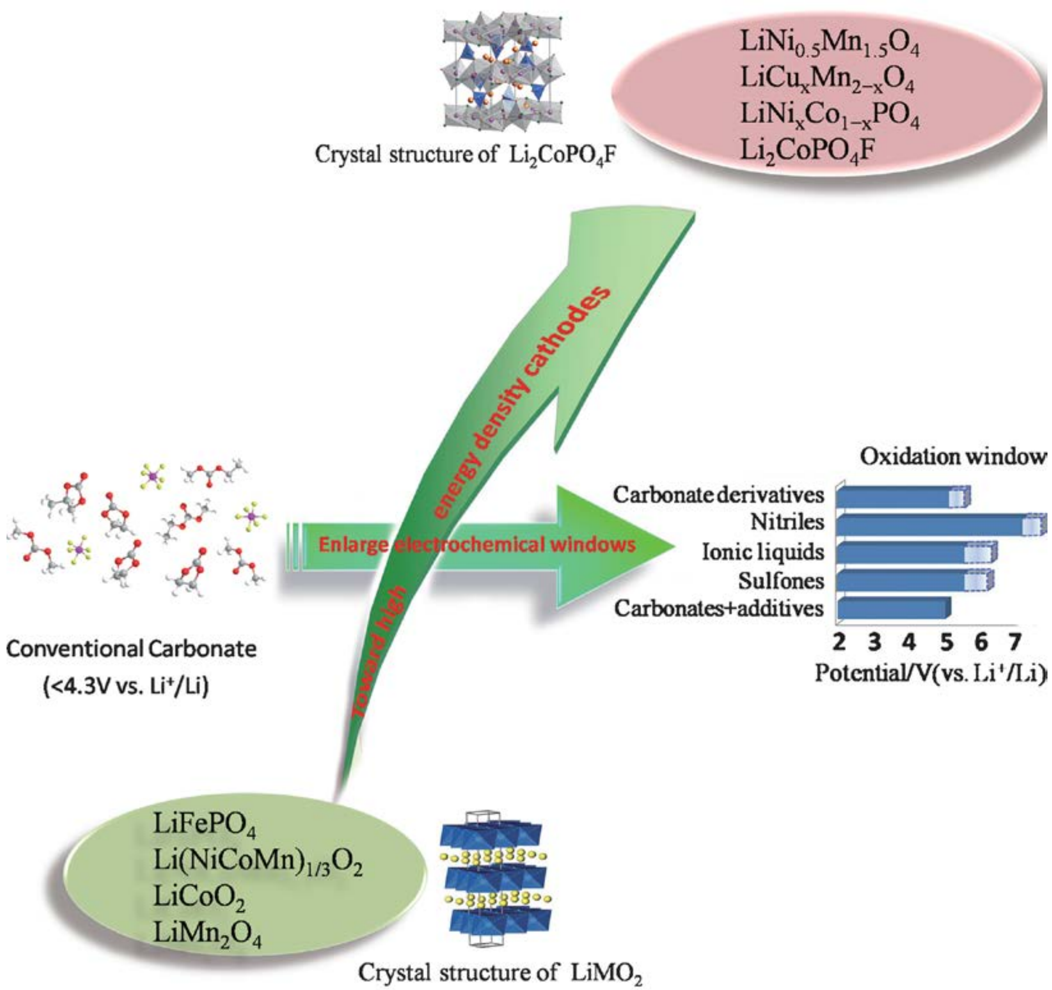
Budget

- Total project funding
  - 100% DOE funding
- Funding received in FY14: $500 K
- Funding for FY15: $500 K

Partners

- U.S. ARL (collaborator)
- BNL (collaborator)
- LBL (collaborator)
- Prof. Brett Lucht (XPS)
- Dr. Marshall Smart (JPL)
- Dr. Larry Curtiss (DFT)

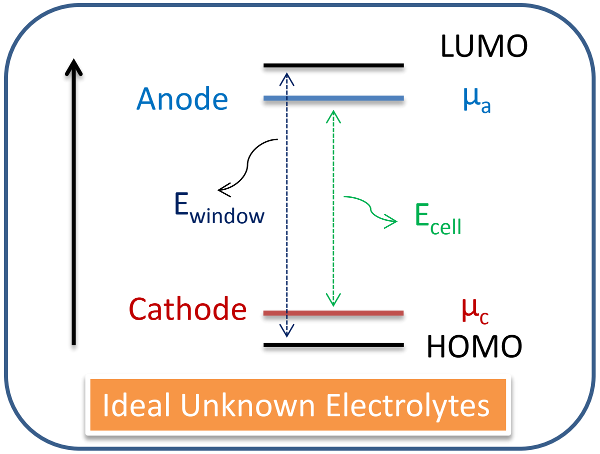
Project Objective

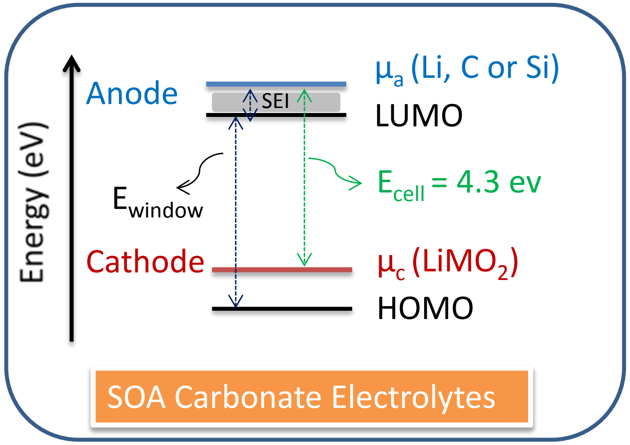


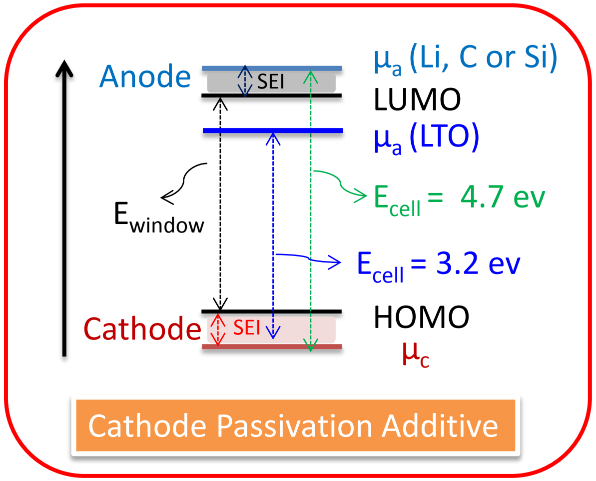
To develop advanced electrolyte materials that can significantly improve the electrochemical performance without sacrificing the safety of lithium-ion battery of high voltage high energy cathode materials to enable large-scale, cost competitive production of the next generation of electric-drive vehicles.

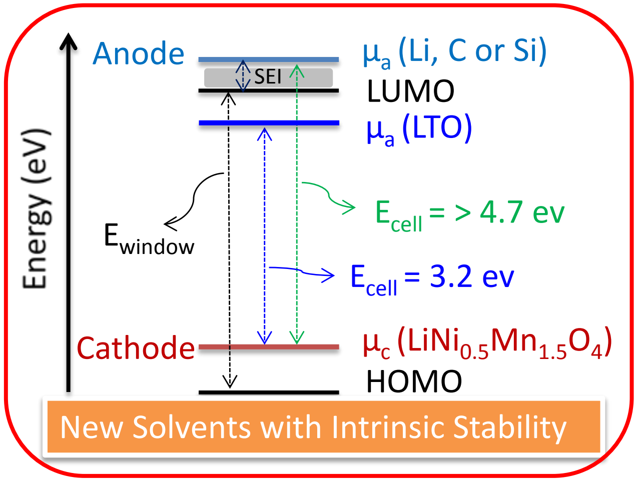
To develop electrolyte materials that can tolerate high charging voltage (>5.0 V vs Li^+/Li) with high compatibility with anode material providing stable cycling performance for high voltage cathodes including 5-V $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathode and high energy LMR-NMC cathode recently developed for high energy high power lithium-ion battery for PHEV/EV applications.

Technical Approach/Strategy







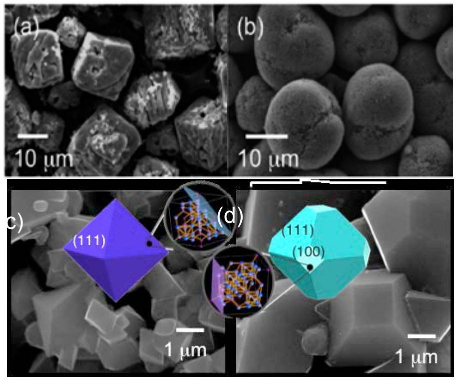


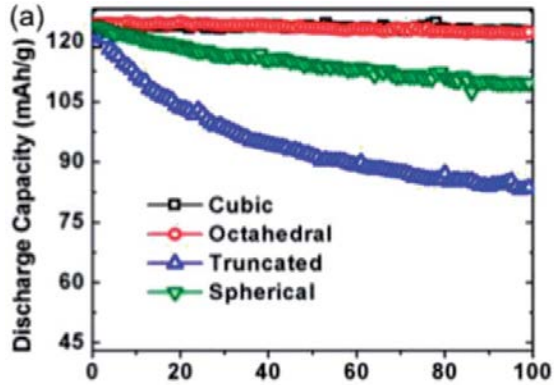
- ✓ Expand the electrochemical window of electrolyte solvents by molecular engineering to enhance the oxidation stability of the electrolyte (5.0 V vs Li^+/Li) without compromising the salt solubility, ionic conductivity, fast ion transportation, wide temperature range and safety.
- ✓ High compatibility with cell component (separator, electrode, binder et al.)
- ✓ SEI formation capability on carbonaceous anode surface.

Technical Accomplishments and Progress

The Challenges for High Voltage $LiNi_{0.5}Mn_{1.5}O_4$ Cells

1. Variations in performance depending on the synthesis process/sintering conditions



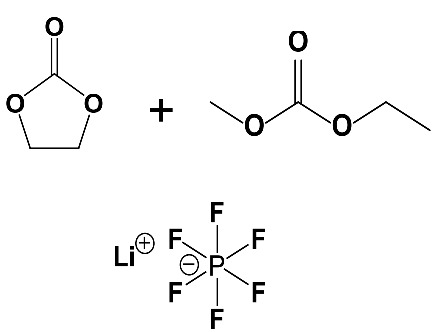


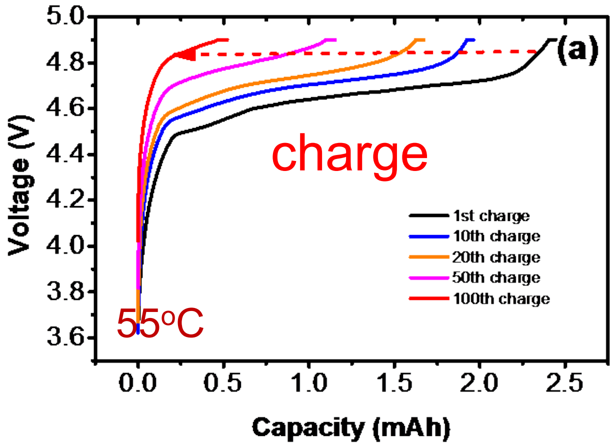
SEM images of $LiMn_{1.5}Ni_{0.5}O_4$ samples prepared by employing various precursors: (a) and (b); Crystallographic planes of (c) octahedral and (d) truncated octahedral spinel synthesized by different synthesis techniques;

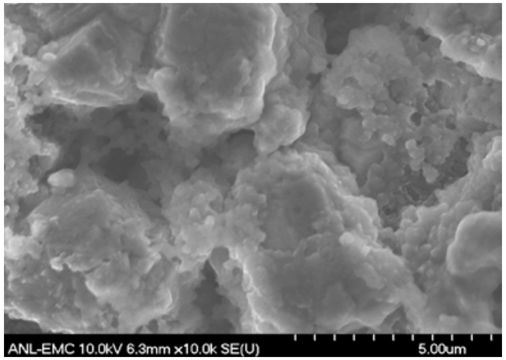
Cycling performance of LNMO cell with various particle morphologies

1) Manthiram et al., *Energy Environ. Sci.*, 2014, 7, 1339; K. Zaghib et al., *RSC Adv.*, 2014, 4, 154-167.

2. Instability of the cathode surface in contact with electrolyte at 4.7 V, especially at high T



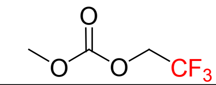
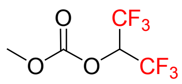
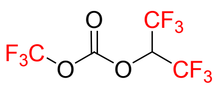
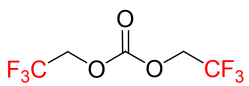
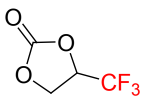
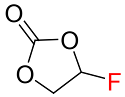
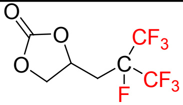
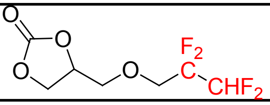




Heterogeneous charging voltage profile and heavy deposition observed on LNMO electrode surface (SEM), indicating the instability of SOA electrolyte at high charging voltage at high temperature.

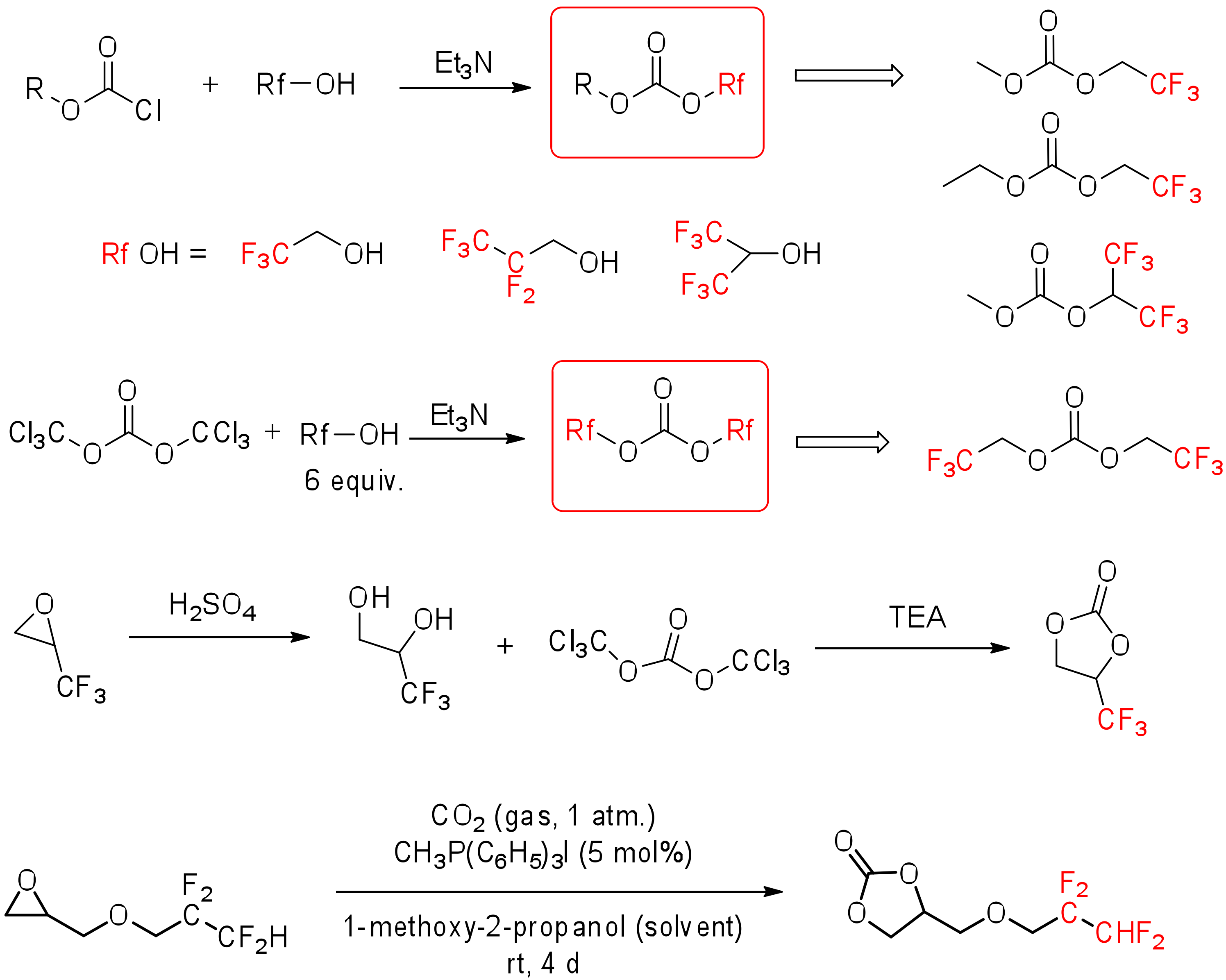
Hu et al., J. Power Sources, 236, (**2013**), 175-180.

Electron-Withdrawing Effect of F- and F-alkyl by DFT

Molecular Structure	Oxidation Potential (P_{ox}/V)	Anion Effect Potential (P_{ox}/V)	Reduction Potential (P_{red}/V)	Stretch Bond Potentials (P_{red}/V)
	7.10 (6.62, EMC)	6.26 (PF_6: HF forms) 5.79 (TFSI: H transfer)	0.03	1.40 (CF_3CH_2-O) 1.49 (CH_3-O)
	7.70 (6.46)	6.28 (PF_6) 5.83 (TFSI)	0.30	
	7.96 (6.46)	7.69 (PF_6) 5.76 (TFSI)	1.29	1.54 (CF_3CH_2-O) 2.39 ($(CF_3)_2CH$-O 1.47 (CF_3-O)
	7.25 (6.51, DEC)	7.35 (PF6) -	0.22	1.65 (CF_3CH_2-O)
	7.30 (6.80, PC)	6.21 (PF_6) 5.33, 5.44, 5.87 (TFSI)	1.54 (spontaneous C-O bond opening)	
	7.24 (6.95, EC)	6.44 (PF_6) 5.80 (TFSI)	0.33	1.56 (CHF-O)
	6.97			
	6.24	6.05 (PF_6) 5.90, 5.19, 5.22 (TFSI)	0.01	1.50

- Electron-withdrawing groups of -F and -R_f groups lower the energy level of the HOMO, thus increase the theoretical oxidation stability of the F-compounds.
- The electron-withdrawing effect varies with the structure and the position of the substitution groups.

Synthesis of Fluorinated Carbonates



F-EMC

TF-DEC

FMiPC

HF-DEC

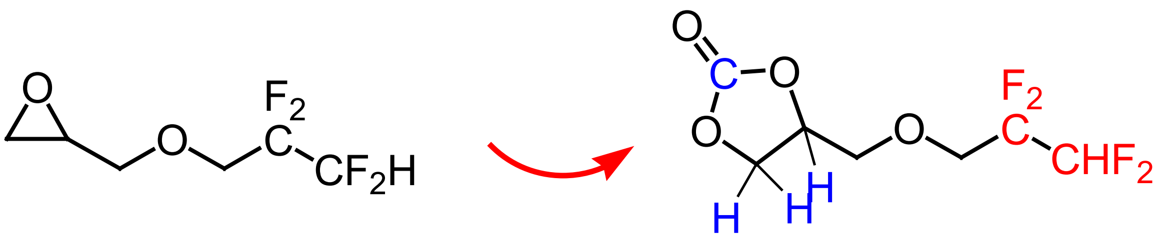
TFPC

TFP-PC-E

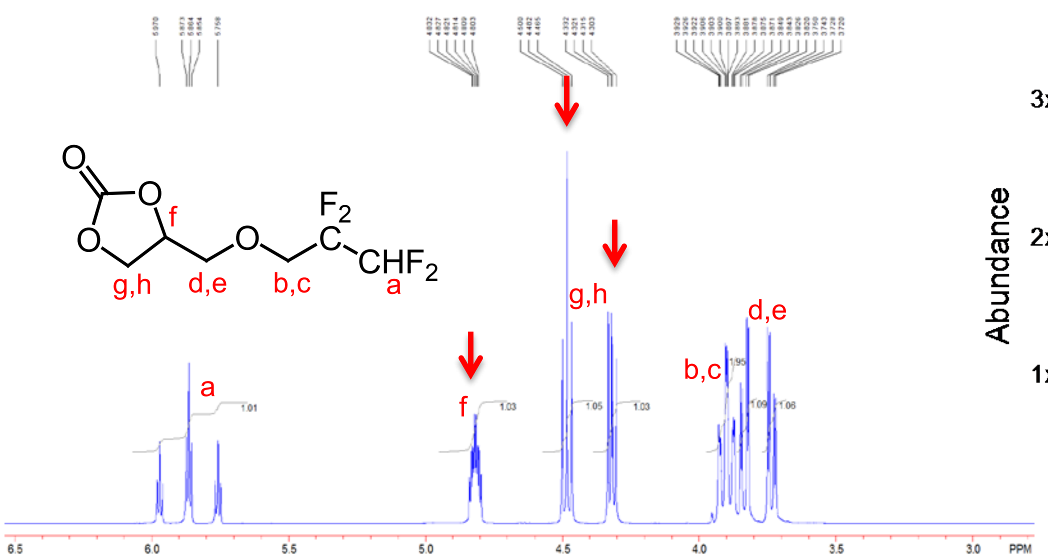
Spectroscopic Characterization and Identification

TFP-PC-E

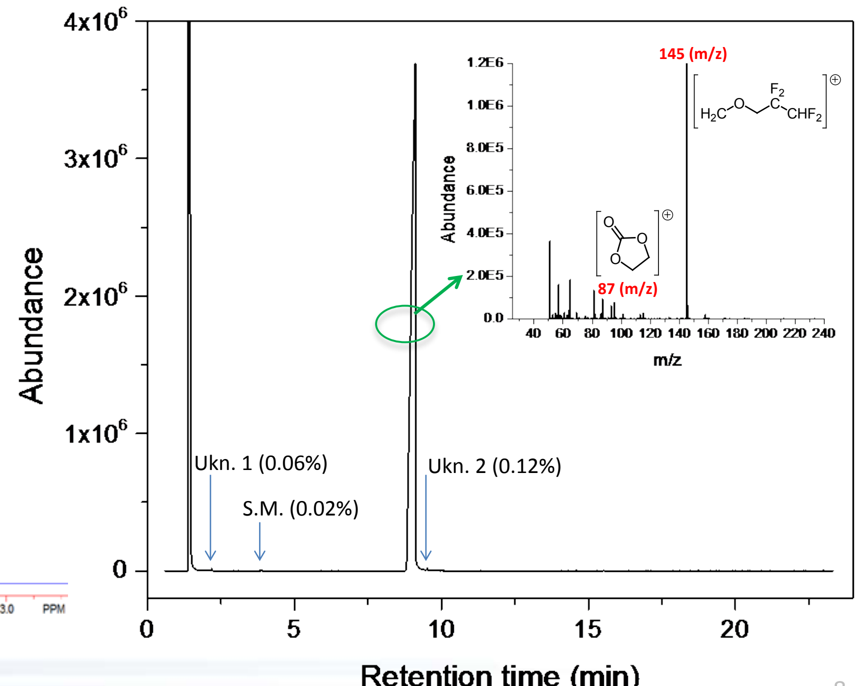
(Tetrafluoropropyl-Propylene Carbonate-Ether)



^{1}H-NMR Spectrum

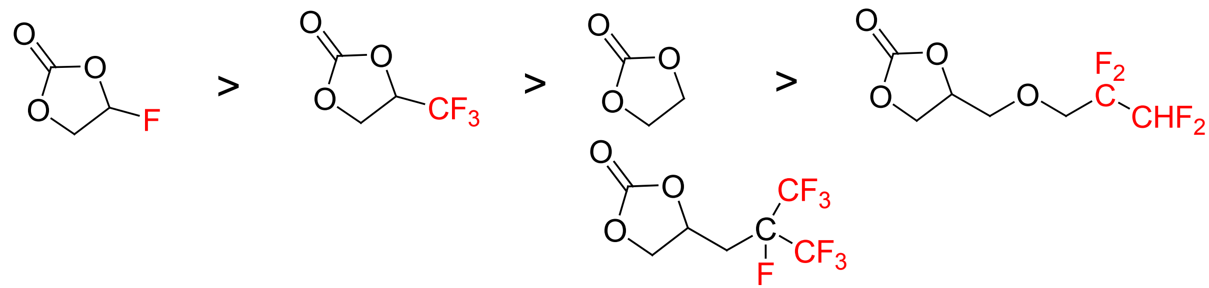


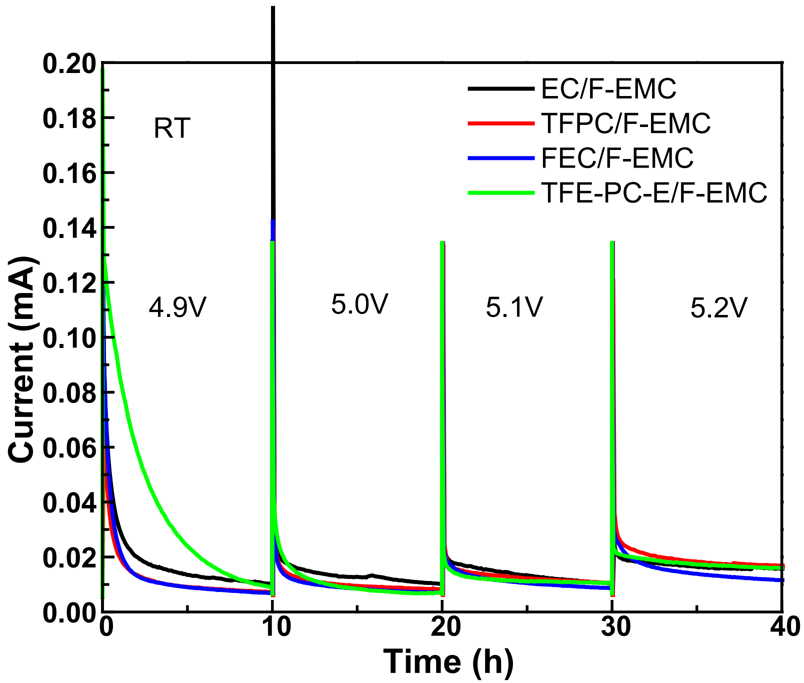
GC-MS Spectrum



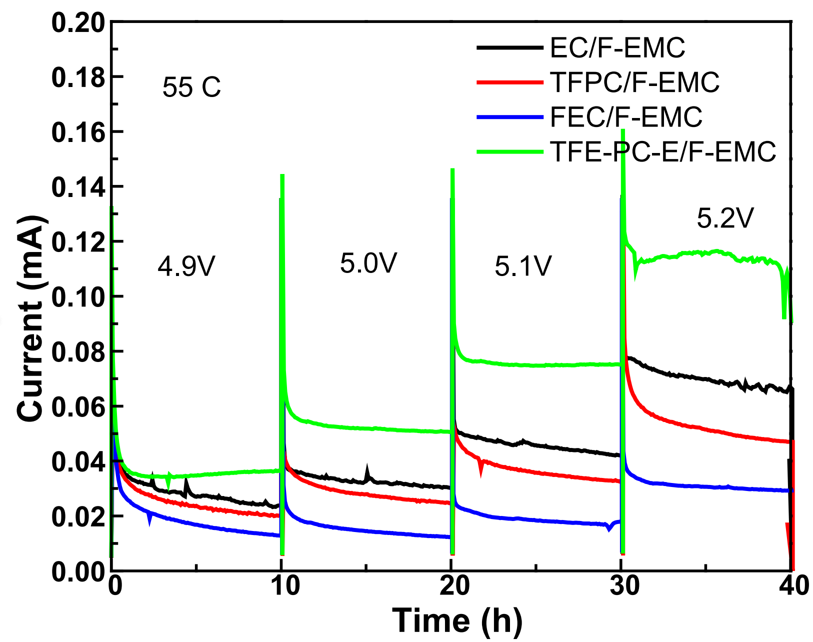
Oxidation Stability of Cyclic F-Carbonates

F-cyclic carbonate oxidation stability: FEC > TFPC > EC > TFE-PC-E





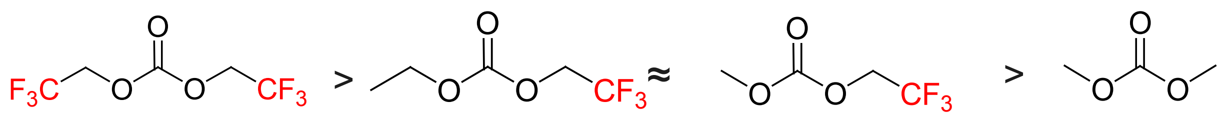
55°C

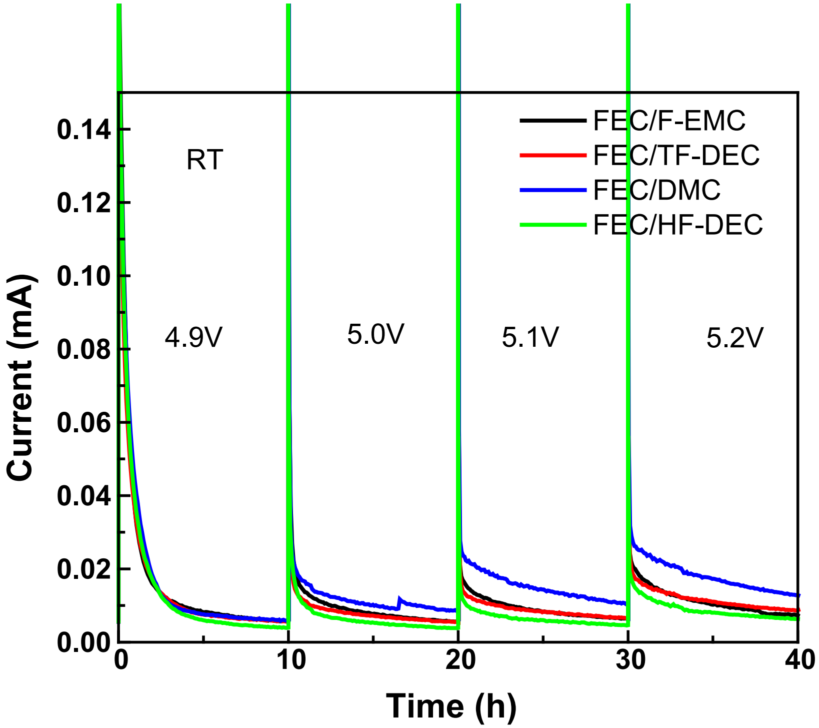


- 0.5M $LiPF_6$ in F-cyclic carbonate/F-EMC=1:1 (v/v); LNMO/Li half cell, fully charged at 4.9, 5.0, 5.1 and 5.2V
- F-electrolyte showed small difference in leakage current at RT; at 55°C, the current increases significantly
- Due to the catalytic reaction at the interface of LNMO/electrolyte at high temperature, EC and TFE-PC-E is extremely unstable.

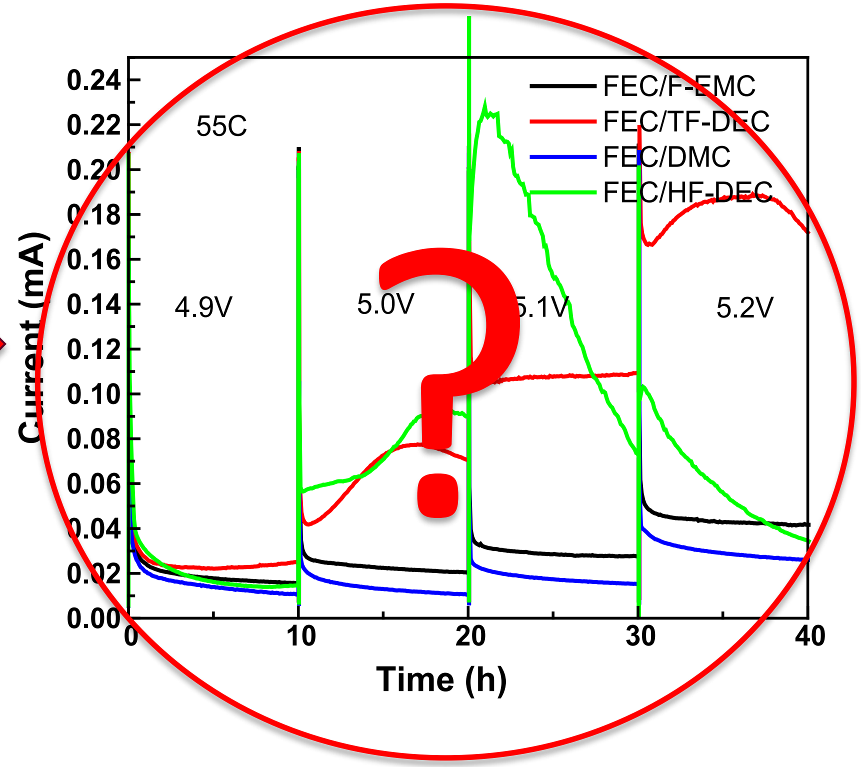
Oxidation Stability of Linear F-Carbonates

HF-DEC > TF-DEC ≈ F-EMC > DMC





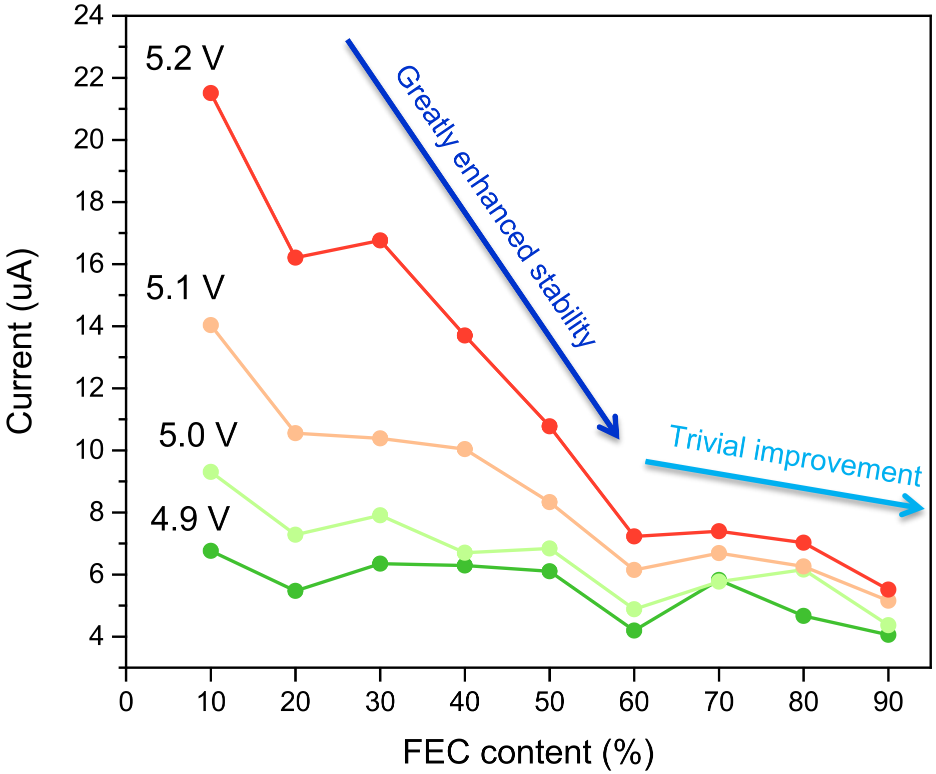
55°C



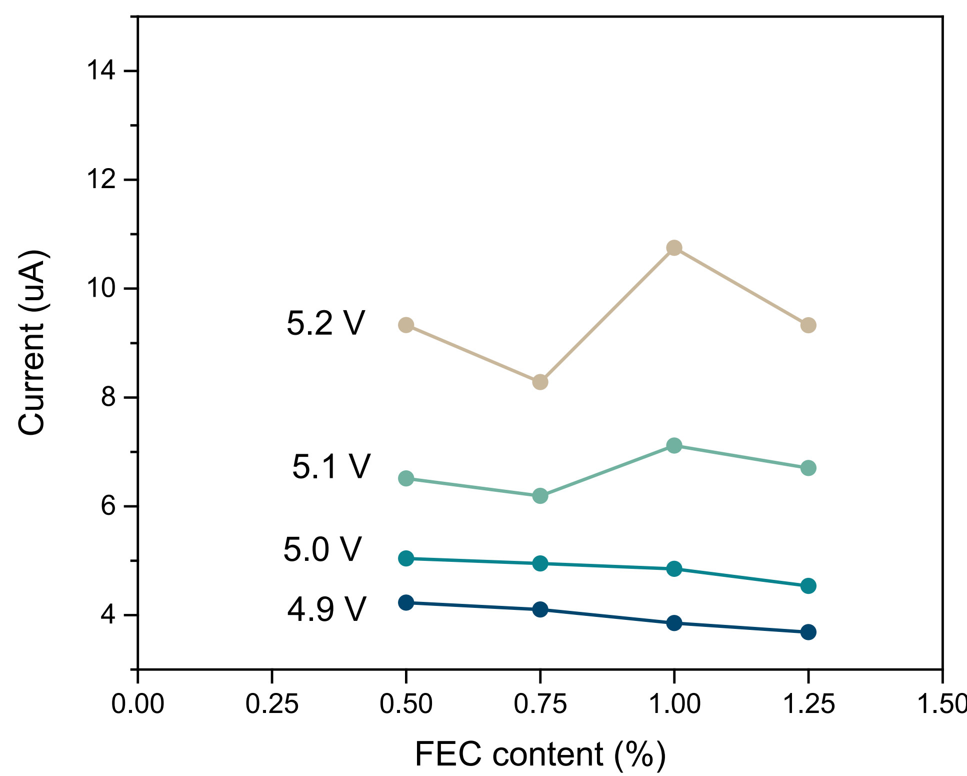
- * Oxidation stability at room temperature; high temperature data deviates from the RT data due to the thermal decomposition.
- 0.5 M $LiPF_6$ in FEC/F-linear carbonate = 1:1 (v/v); LNMO/Li half cell, fully charged at 4.9, 5.0, 5.1 and 5.2 V at RT and 55°C.

Mixed Solvent Ratio and Salt Concentration on Oxidation

0.5 M $LiPF_6$ in FEC:DMC (from 1:9 to 9:1)



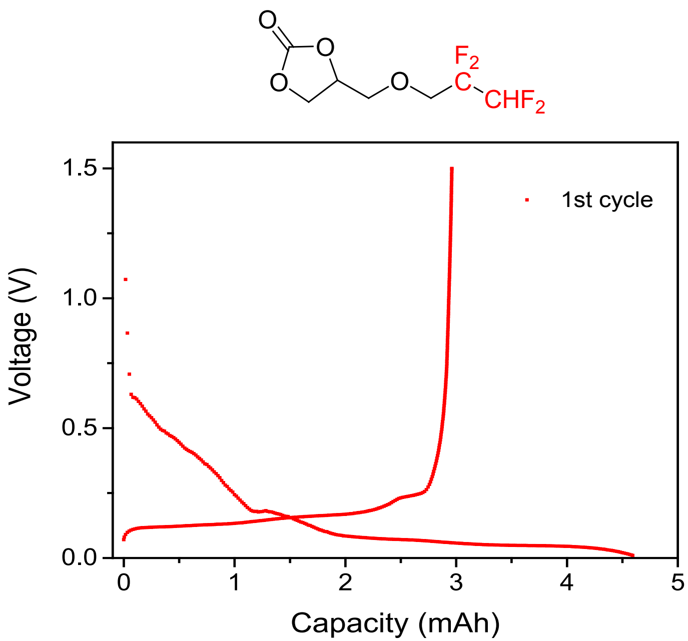
FEC:DMC = 5:5 with $LiPF_6$ from 0.5 M to 1.25 M

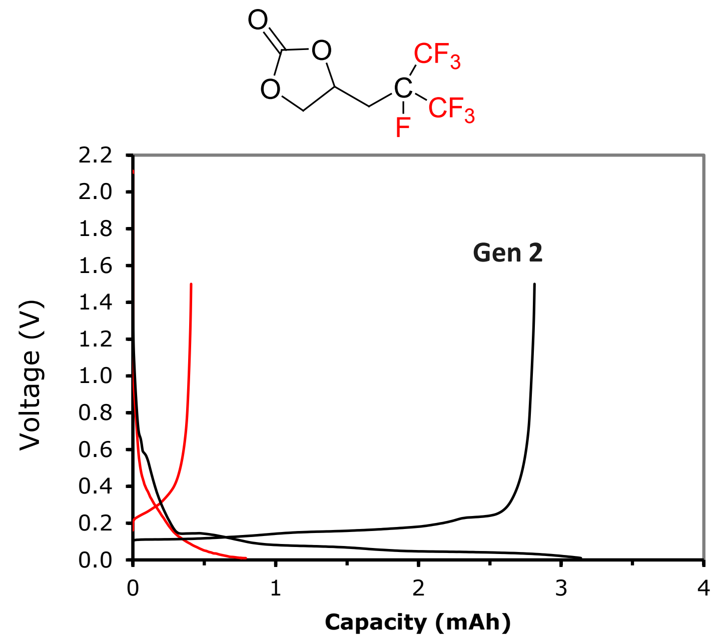


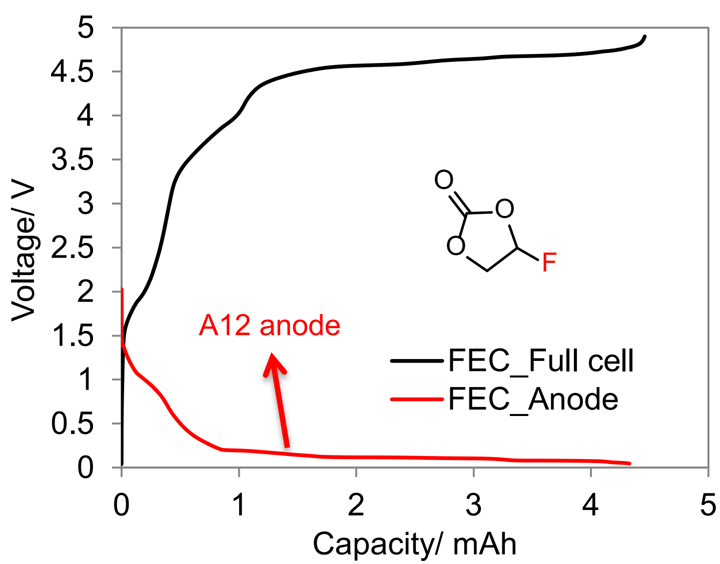
FEC content affects the voltage stability at high charge voltages, but less significant at lower voltages (4.9 and 5.0V)

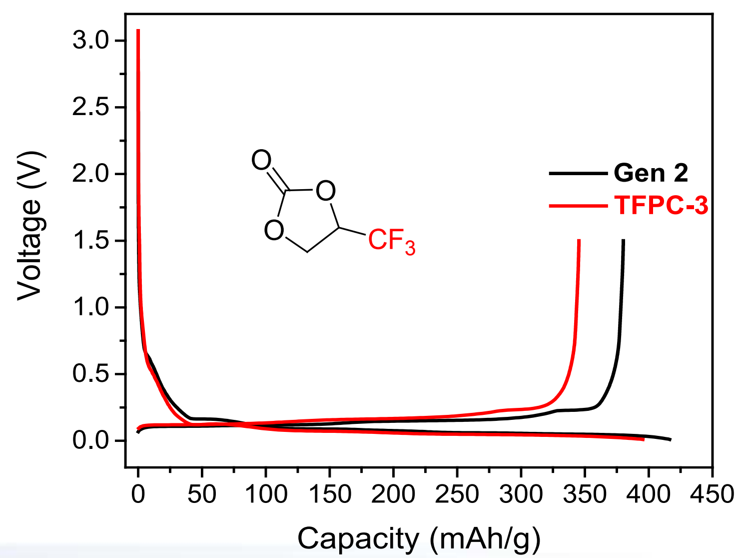
No significant effect of $LiPF_6$ salt concentration on voltage stability, especially at charge voltages below 5 V.

Compatibility of Electrolytes with Graphite Anode

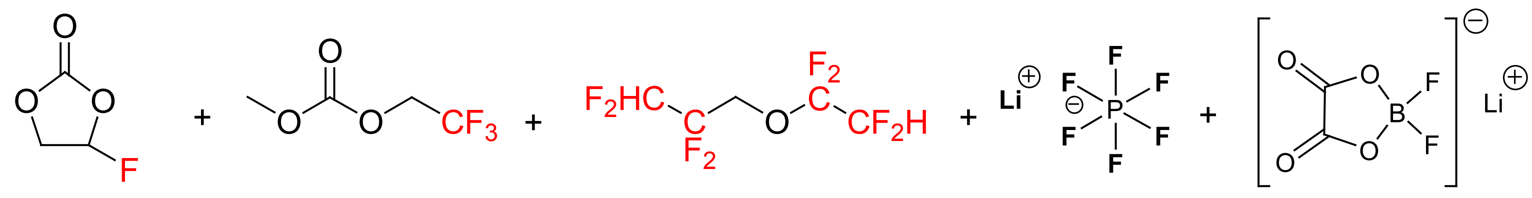




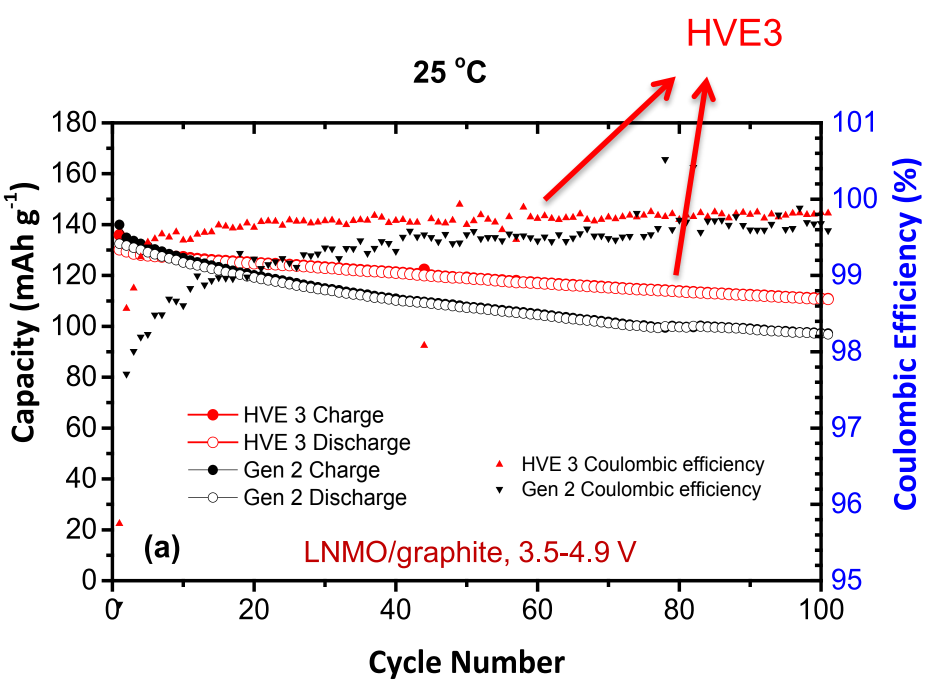


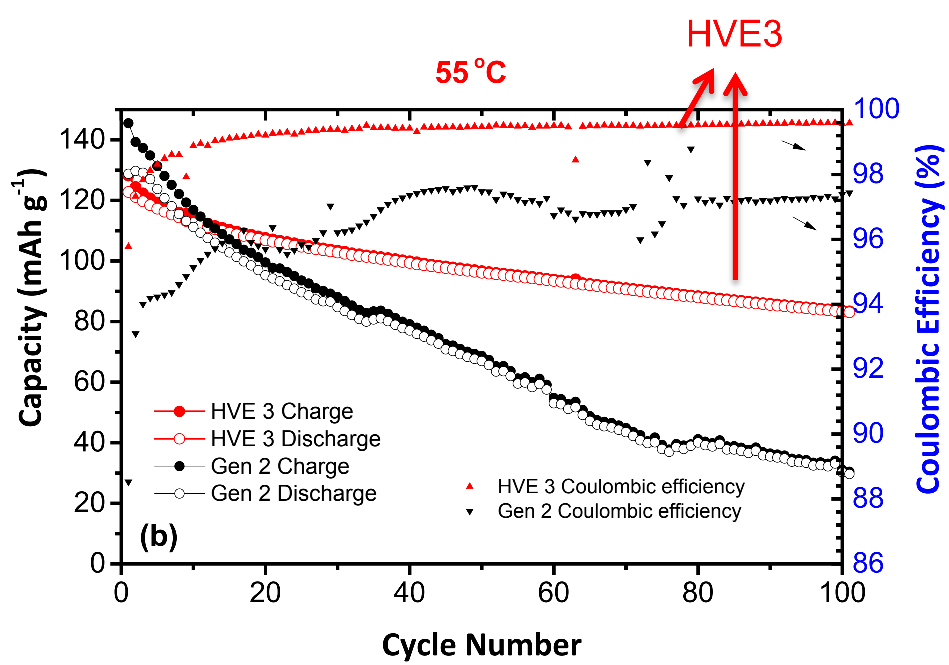


Fluorinated Electrolyte for LNMO/Graphite Full Cell



F-EC(3) F-EMC(5) F-EPE(2) $LiPF_6$ (1.0 M) LiDFOB (1%)





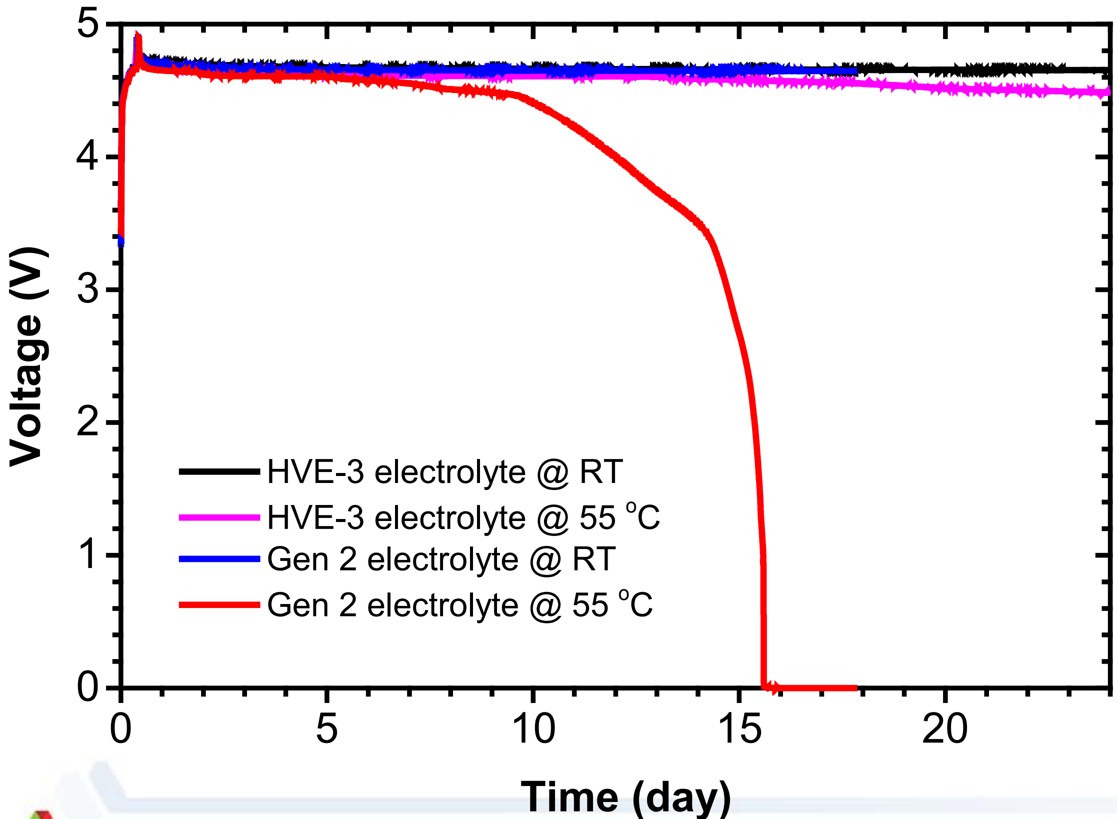
HVE 3 shows great compatibility with graphite surface as indicated by the improvement in LNMO/graphite cells compared with Gen 2 electrolyte, especially at 55 ºC.

Hu, Zhang et al. *Electrochem. Commun.*, **2013**, *35*, 76.

Improved Self-Discharge of LNMO/Graphite Cells

Cathode: $LiNi_{0.5}Mn_{1.5}O_4$
Anode: Graphite A12
Formation condition: 3.5-4.9 V for 3 cycles, C/10 rate at RT

Self-discharge Test: fully charge to 4.9 V at C/10 (RT or 55 °C), then rest and monitor the voltage change. Data points are taken every 5 minutes.



Gen 2: SOA electrolyte ($1.2M\ LiPF_6$ EC/EMC 3/7 in weight ratio)

HVE-3*: 3rd Generation high voltage F-electrolyte ($1.0M\ LiPF_6$ FEC/FEMC/F-EFE 3/5/2 in volume ratio

** Ref: Hu & Zhang Electrochem. Commun. 35 (2013) 76-79.*

Fluorinated Electrolytes are Not Flammable

Gen 2

Video Here

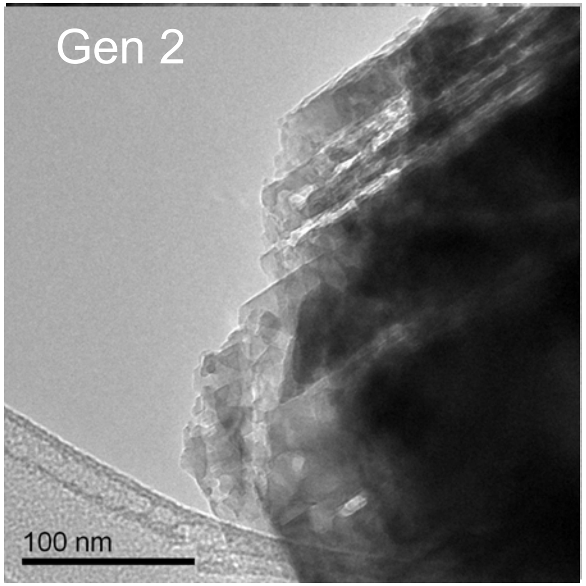
$1.2M\ LiPF_6$ EC/EMC 3/7 weight

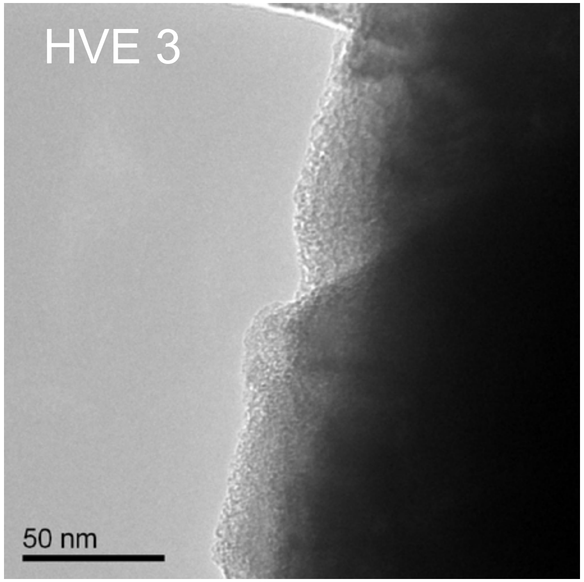
HVE 3

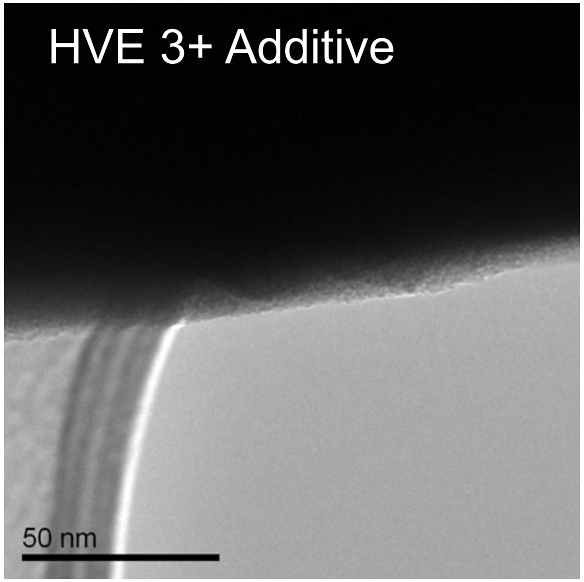
Video Here

$1.0M\ LiPF_6$ FEC/F-EMC/F-EPE 3/5/2 in volume

TEM Characterization of Cycled LNMO Cathode

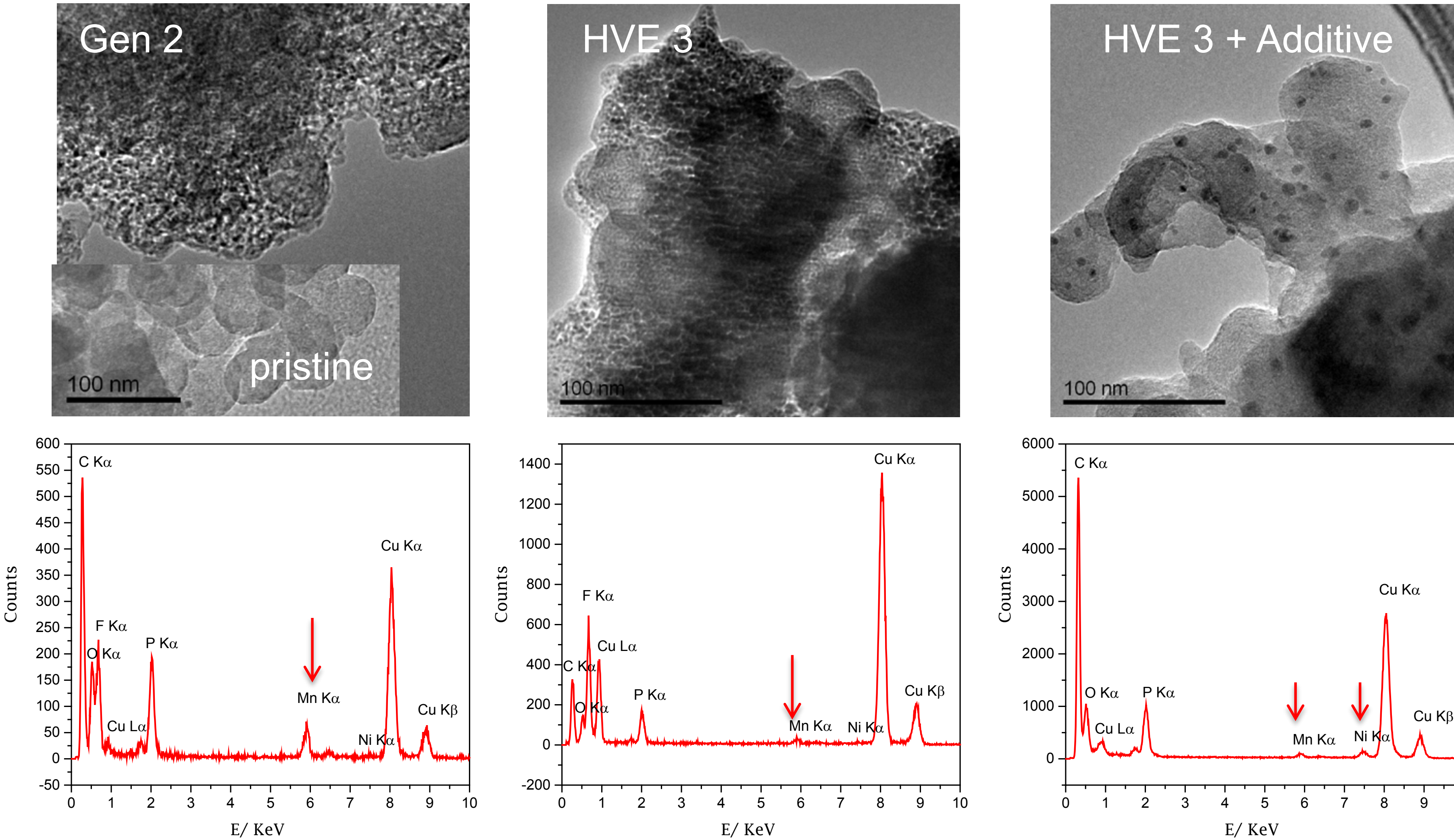






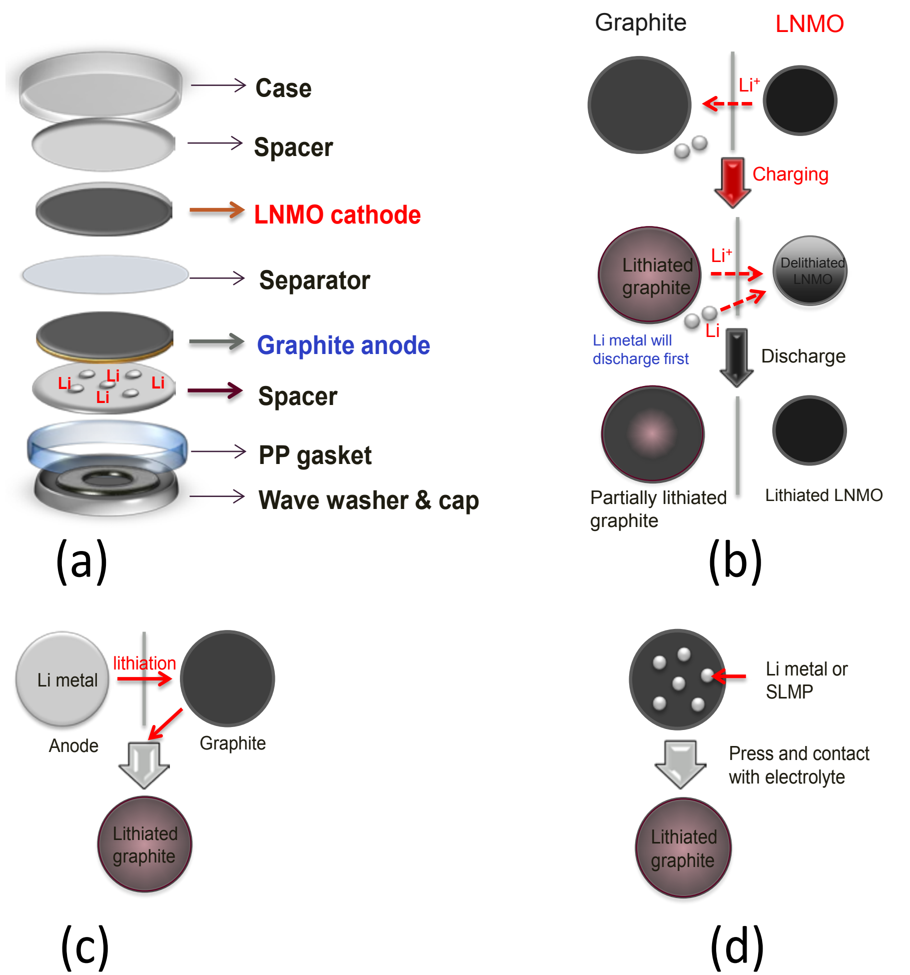
- Etching of LNMO particles is pronounced in baseline cell due to the oxidative decomposition of EC-EMC solvents and the generation of HF leading to Mn and Ni dissolution.
- Mn and Ni exist in the cycled baseline electrolyte with much higher concentration (ICP-MS data, not shown).
- LNMO surface is intact with HVE electrolyte, and more integrated when LiDFOB additive was employed, indicating the improved chemical and electrochemical stability of F-electrolyte.

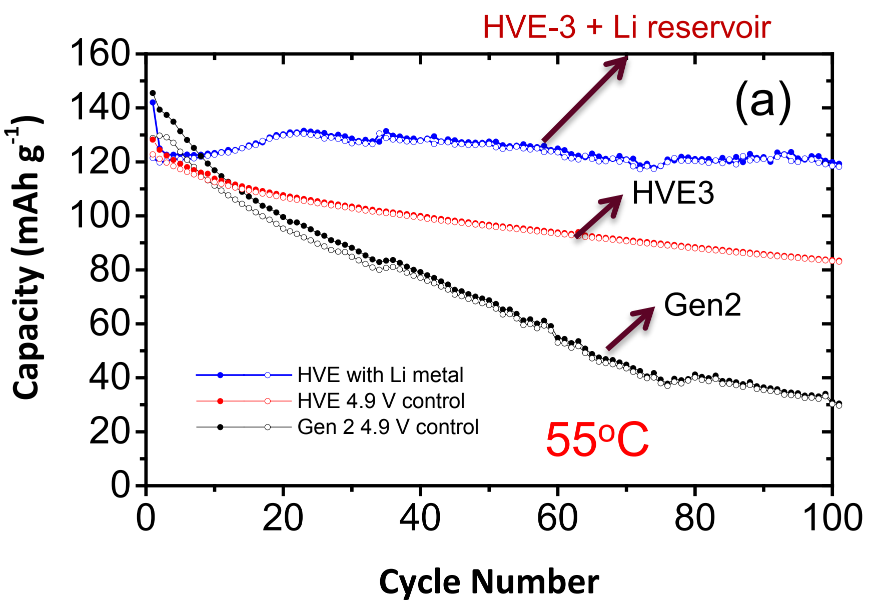
TEM Characterization of Graphite Anode

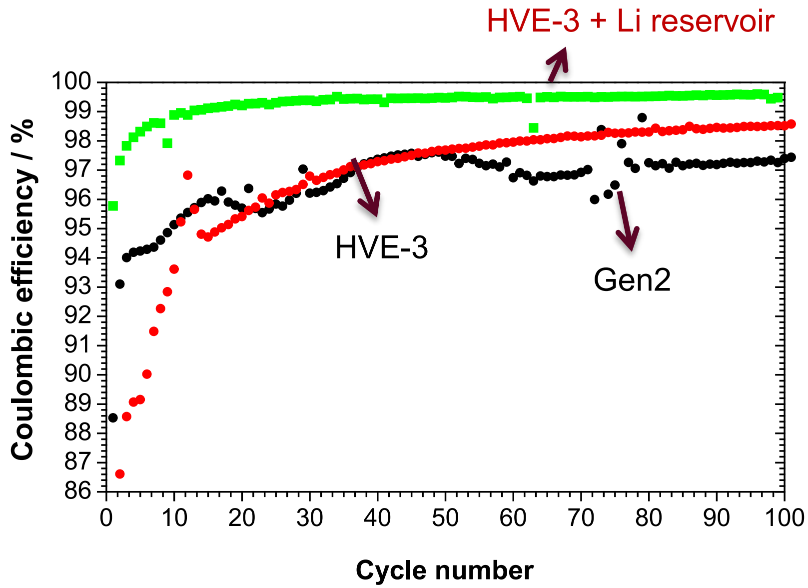


- Anode of Gen2 cell showed significant amount of nanoparticles (a few nm) of transitional M species in the carbon black region, which might catalyze the parasitic reactions.
- However, anode of HVE3 + Additive cell showed quite different morphology of the transition M: less amount and deposition/agglomeration (~10nm), less catalytic effect leading to less reductive decomposition of electrolyte.

Compensation of Lithium Loss by a Lithium Reservoir



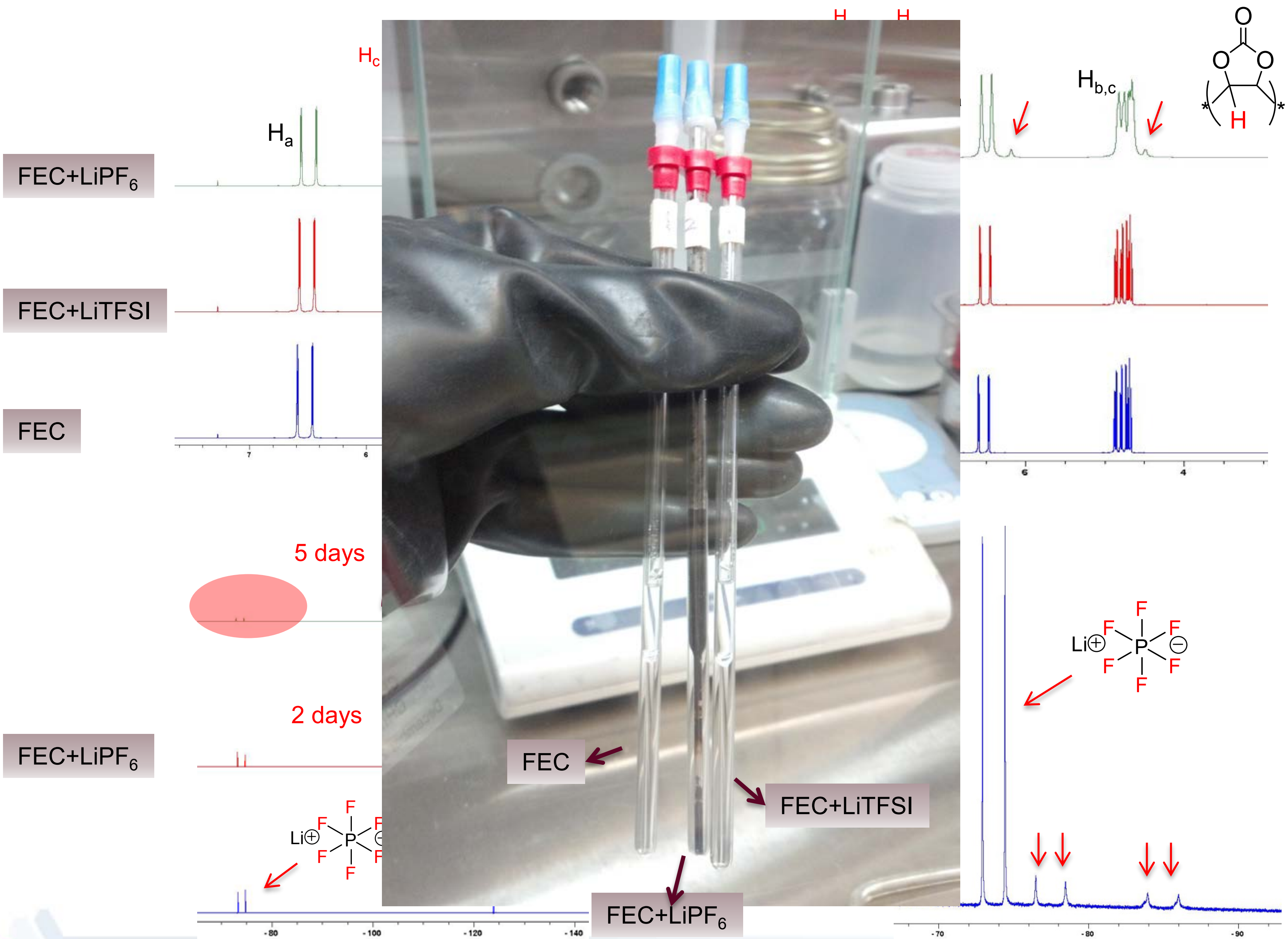




(a) LNMO/graphite cell assembly with incorporated lithium metal; (b) lithium metal working mechanism at the formation cycles; (c) electrochemical prelithiation of graphite anode; (d) direct shorting of graphite anode and Li.

Hu & Zhang *et al.*, *Electrochem. Commun.*, **2014**, *44*, 34-37.

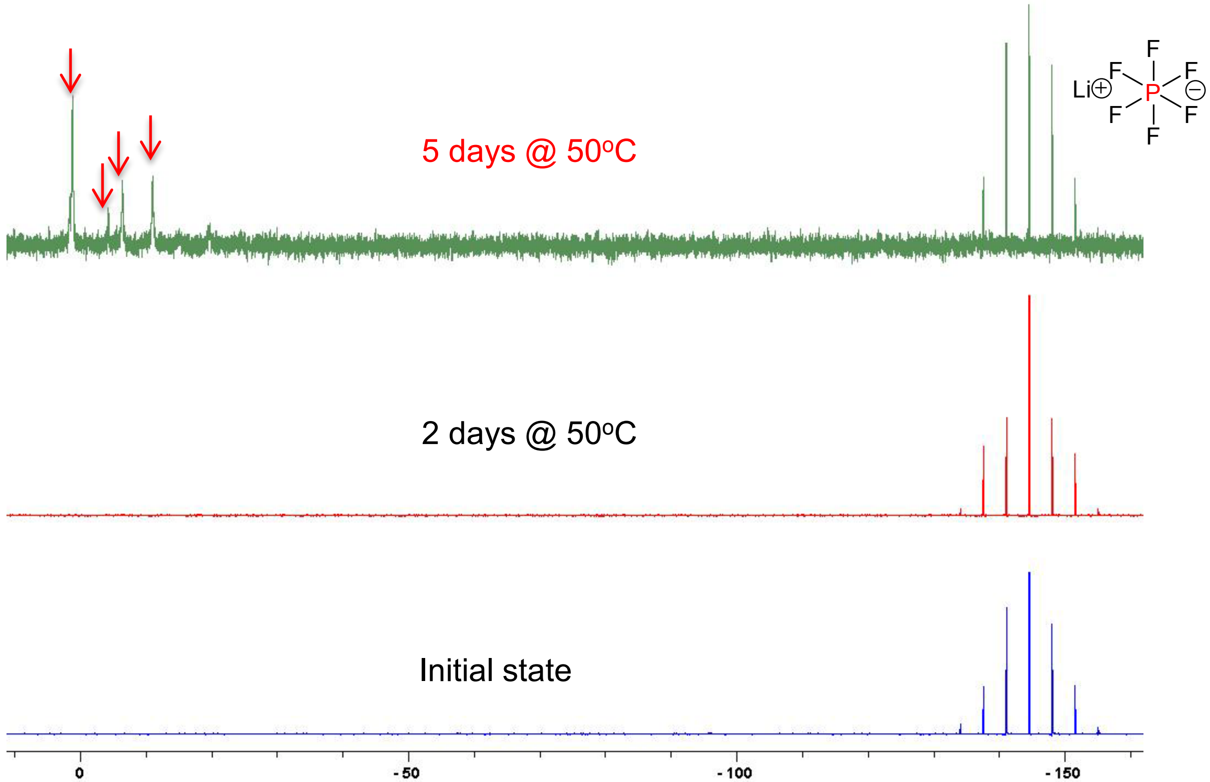
Thermal Stability of FEC-Based Electrolytes: An NMR Study



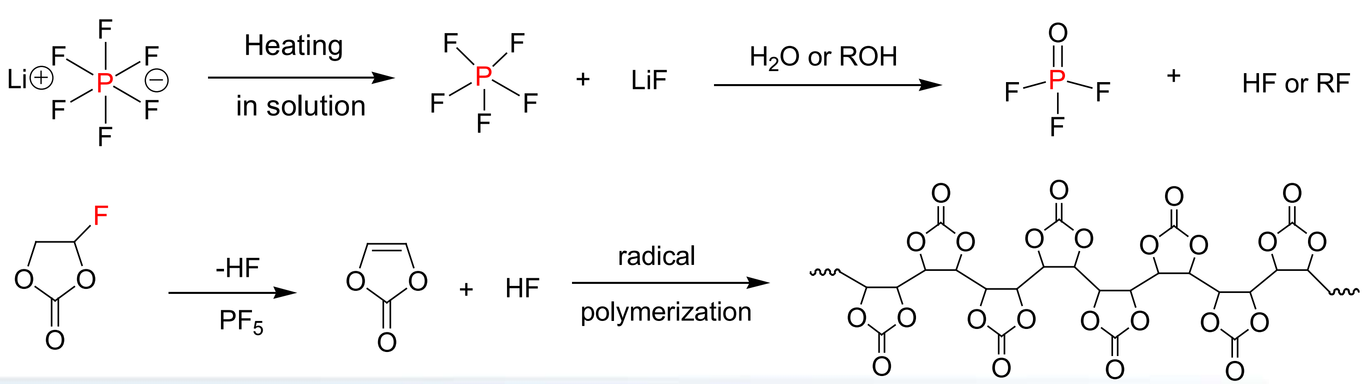
Thermal Stability of FEC-Based Electrolytes

^{31}P-NMR

0.5 M $LiPF_6$
in FEC

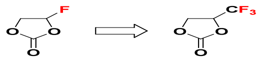


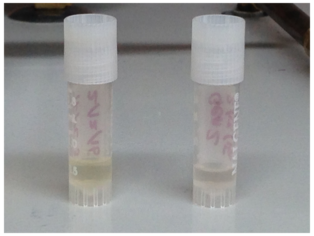
Proposed FEC Thermal Decomposition Pathway:

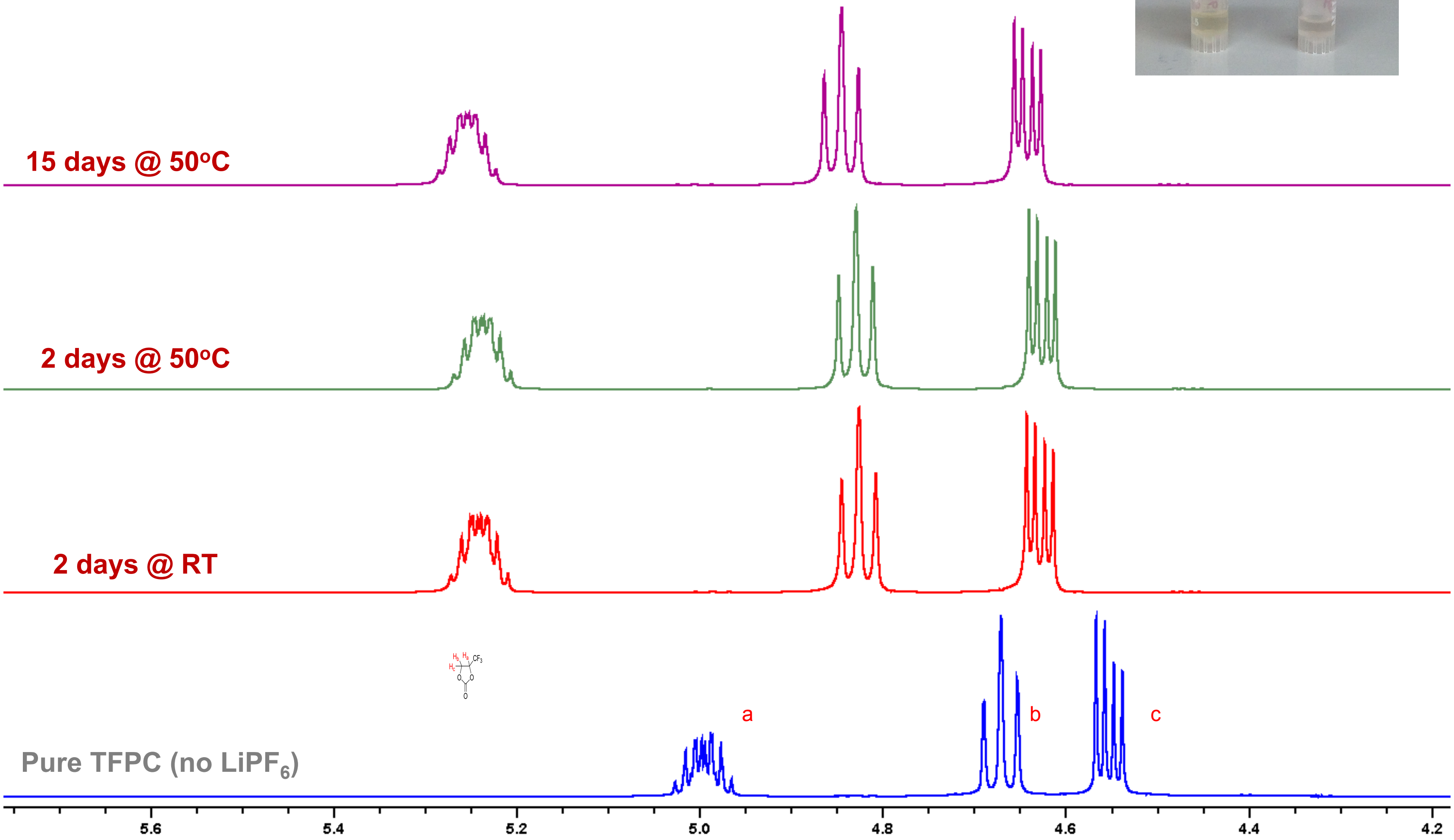


Thermal Stability of TF-PC Based Electrolytes

Method: 1 M $LiPF_6$ in TFPC, heated @ 50 °C for 15 days

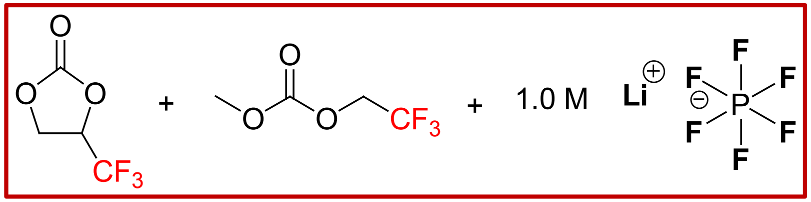


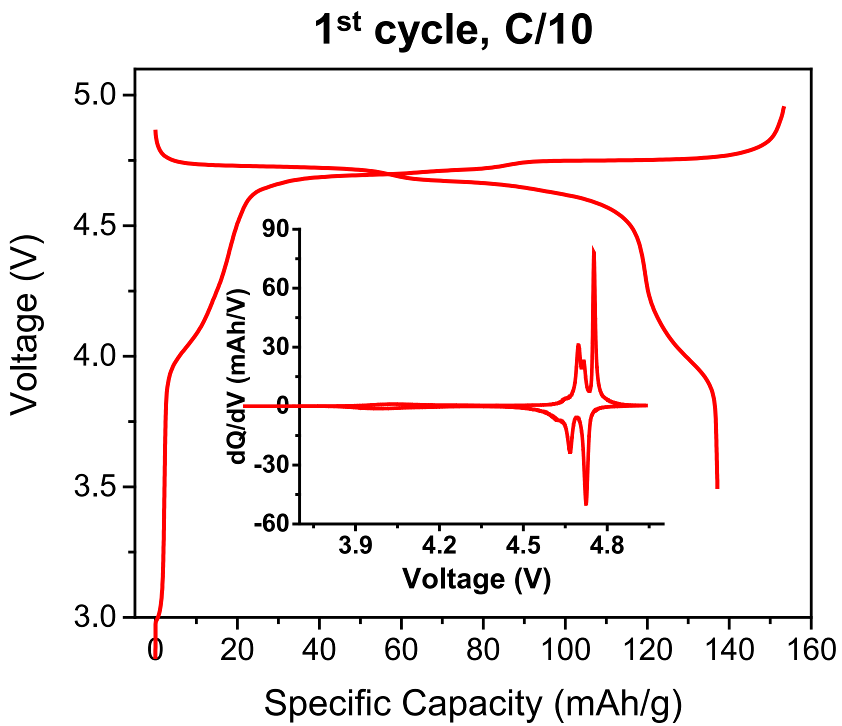


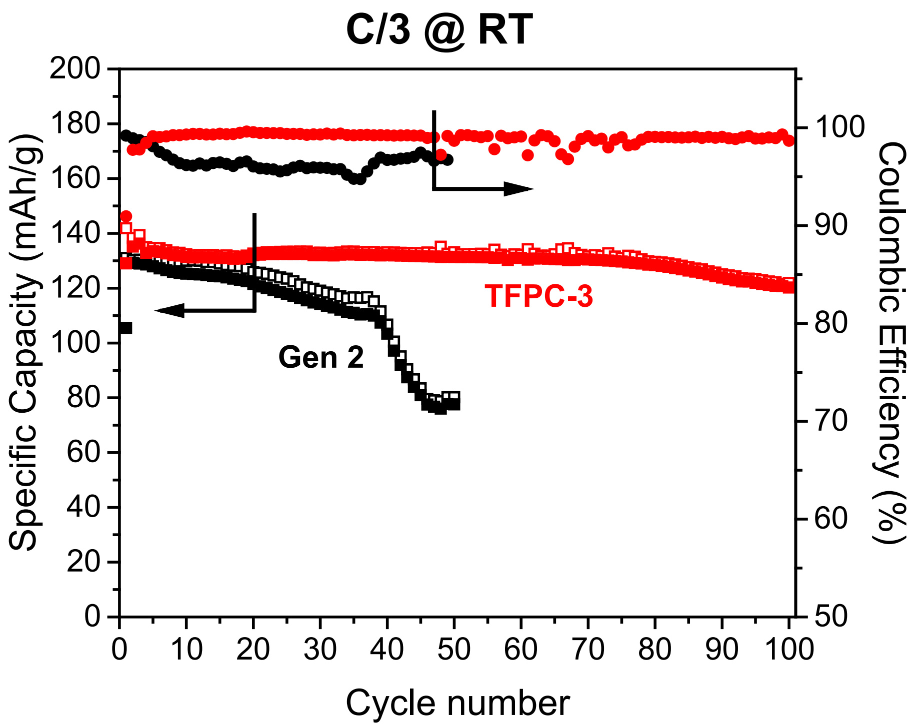


[1]H NMR spectra of TFPC-3 electrolyte from harvested LNMO/graphite cells; TFPC remained stable during cycling at high temperature.

Cell Performance of TF-PC Based Electrolyte TFPC-3

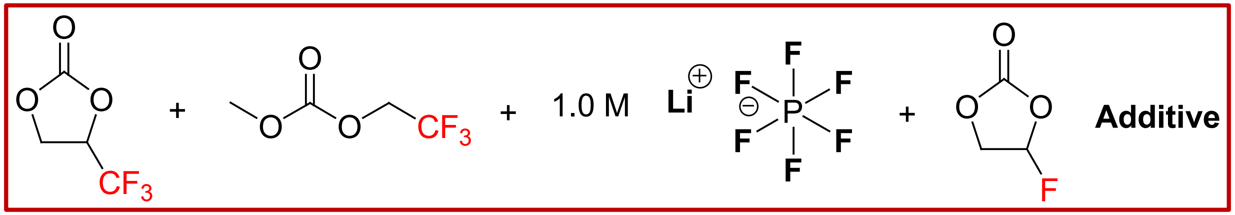


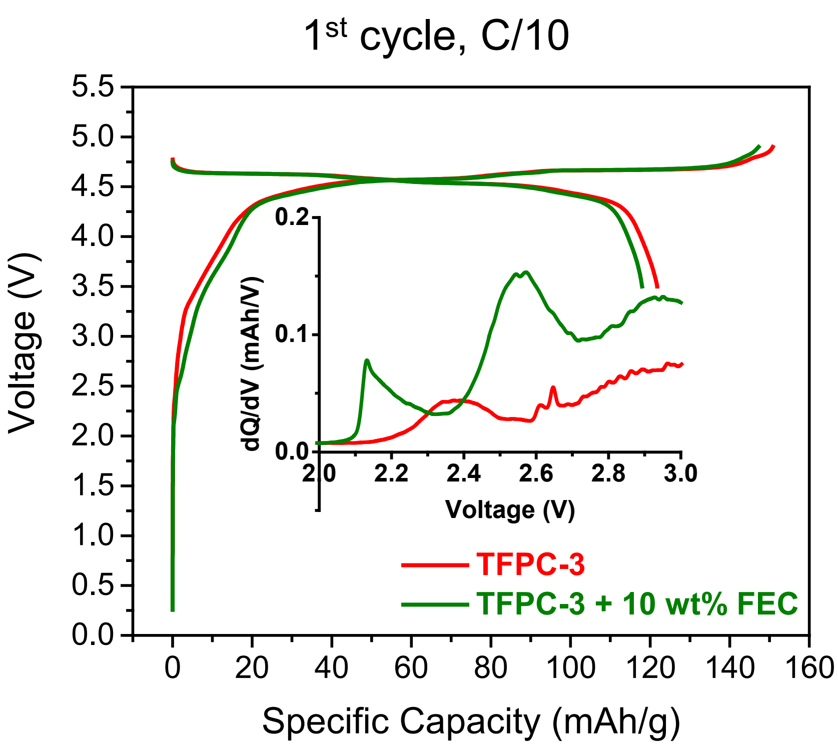


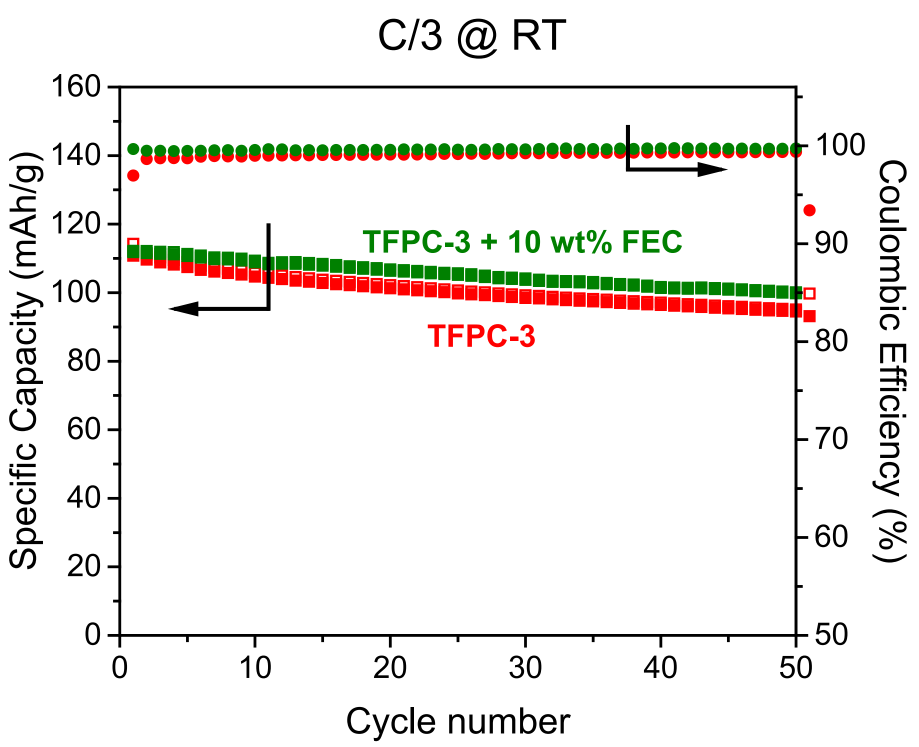


- ❑ LNMO/Li half-cell with TFPC-3 electrolyte performs much better than the baseline cell
- ❑ Improved oxidation stability on LNMO
- ❑ Passivation of Li metal anode due to the thermodynamic instability

RT Cell Performance of TF-PC Based Electrolyte TFPC-3

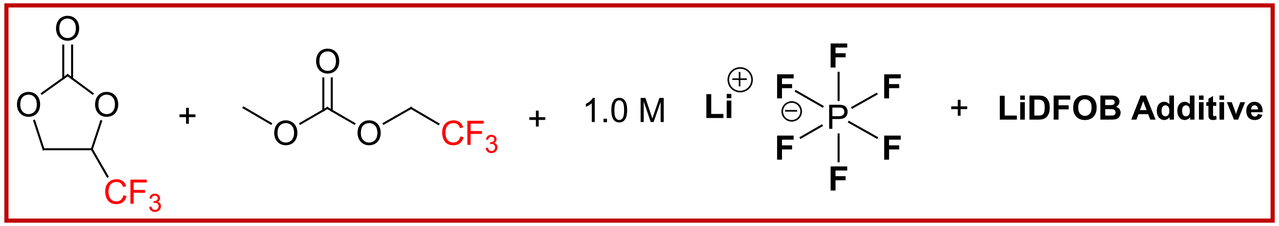


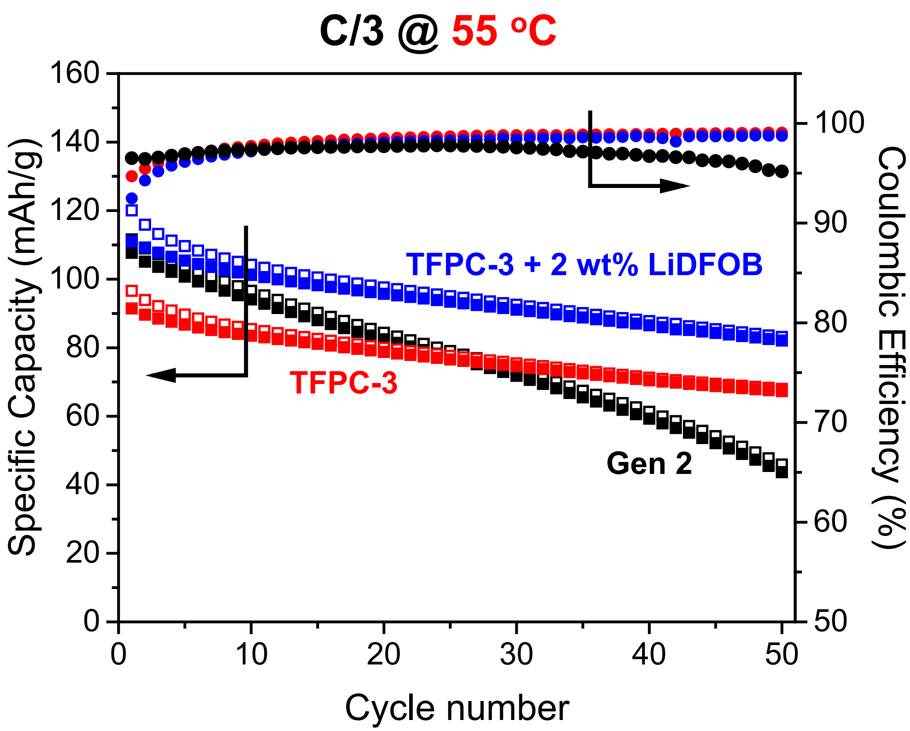


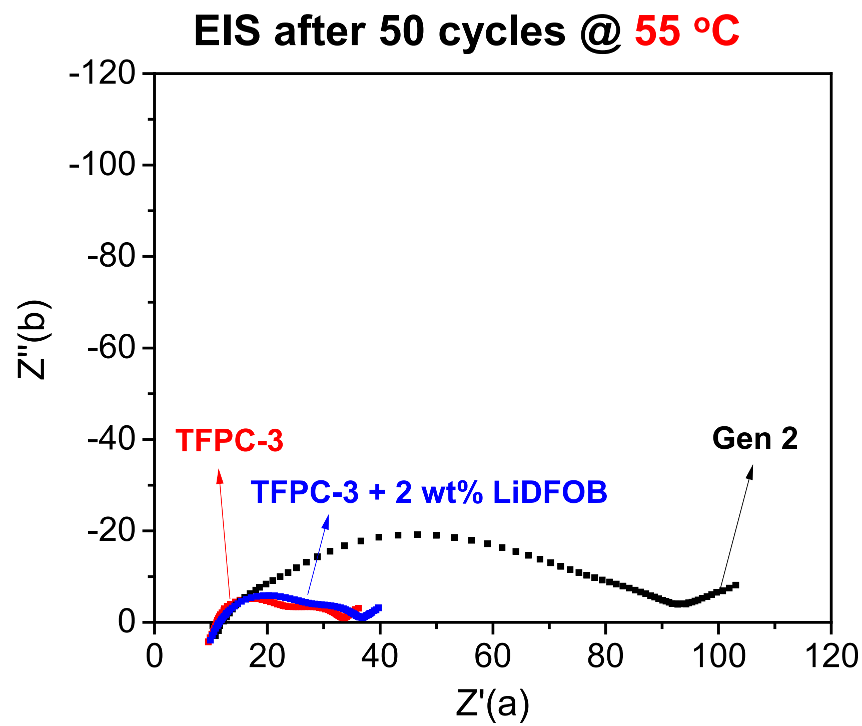


Presence of FEC as an additive in the TFPC electrolyte may promote the formation of a more stable SEI on graphite

TF-PC Based Electrolyte for LNMO/Graphite Cell at HT





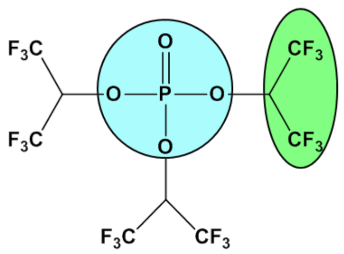


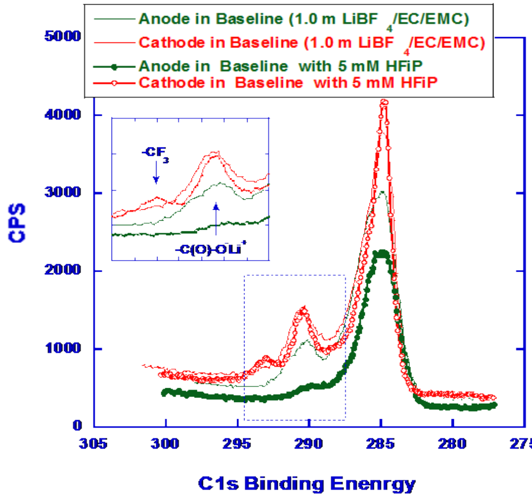
- LNMO/A12 cells with TFPC-based electrolyte exhibits improved capacity retention at 55 °C, which is attributed to the superior oxidation stability of TFPC during high-temperature cycling.
- New formulations and additives for TFPC-based electrolyte is ongoing.

ARL Tasks: Novel Additives

- Design of new additive/co-solvent structures
- Synthesis, purification and structural characterizations
- Electrochemical characterizations
- Fundamental understanding of interphasial process

	DOE BATT	ARL
FR 14	$100K	$100K
FR 15	$100K	$100K





HR-XPS conducted on both cathode and anode cycled in baseline and HFiP-containing electrolytes

- P 2p absent in control samples
- P2p on test samples
  - 5~10 X more on cathode than anode
- C1s for CF_3 only found on cathode

The fate of phosphate in electrolyte

- Phosphate ends up on cathode and anode
- Fluorinated alkyls substructure on cathode

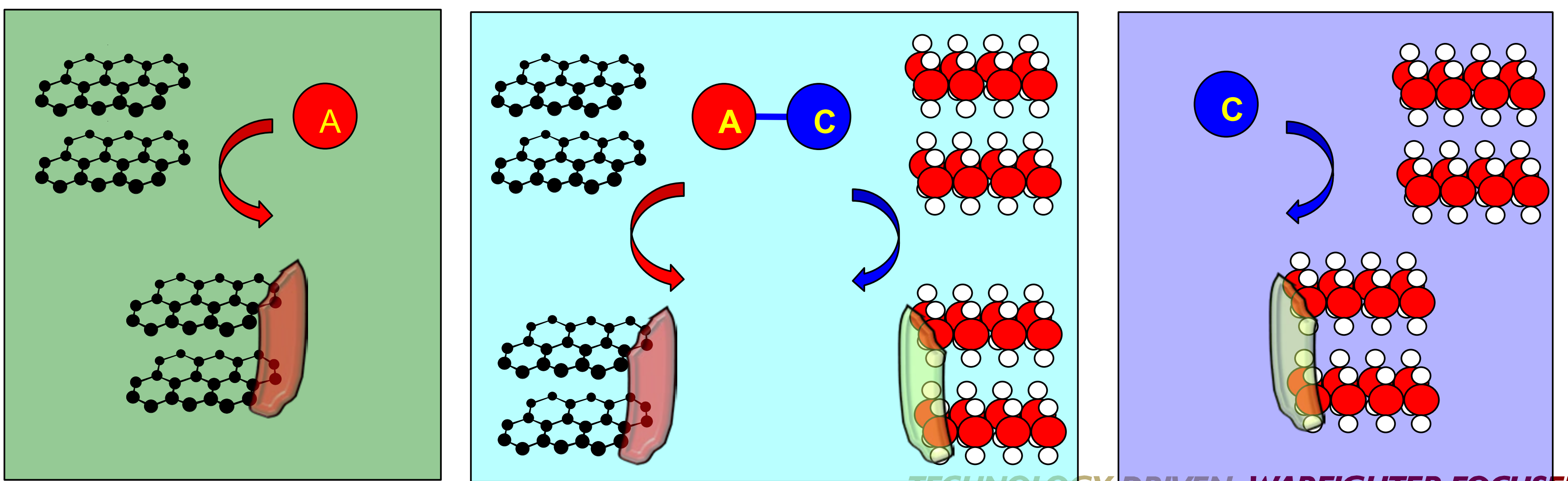
A. v. Cresce, S. M. Russell, O. Borodin, D. Tran, K. Xu

Electrochemistry Branch, Army Research Lab, Adelphi, MD 20783

Philosophy for New Additives Structure

Design Concept:

- Additives interact with both cathode and anode in the cell
- Conventional approach: cathode-specific or anode-specific; cocktail
- Hollistic approach: key structural elements that are effective in forming either cathode or anode SEIs are synthetically-integrated in the same molecule
    - Both high HOMO and low LUMO

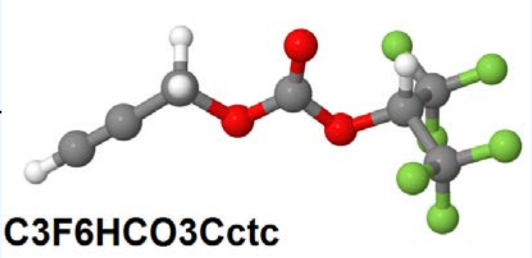


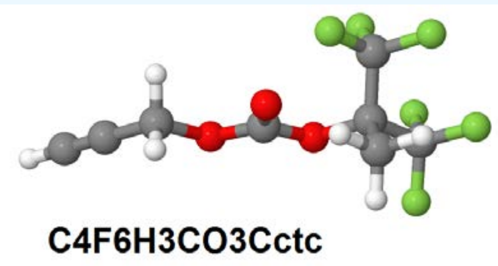
Design Strategy for New Additives

Computational Aid (Borodin):

- QC prediction of HOMO/LUMO can be both very accurate
- Reduction and oxidation potentials cannot predict the consequent interphase chemistry and properties

B3LYP/6-31+G** optimization, gas-phase not PCM			eV	eV	
	O	V	HOMO	LUMO	SMILES
112/CCO3CCC-B3LYP-631xGss.out	-0.29624	0.00664	-8.06	0.18	COc(=O)OCCC (MePrCO3)
22/CCO3Ccc-B3LYP-631xGss.out	-0.28179	-0.01912	-7.67	-0.52	COc(=O)Occc
14/CCO3Cctc-B3LYP-3631xGss.out	-0.28822	-0.00968	-7.84	-0.26	COc(=O)OCc#c
23/C4F6H3CO3Cctc-B3LYP-4631xGss.out	-0.29754	-0.02028	-8.10	-0.55	C(C)(C(F)(F)(F))(C(F)(F)(F))Oc(=O)OCc#c
5/C4F6H3CO3Ccc-B3LYP-5631xGss.out	-0.29177	-0.02851	-7.94	-0.78	C(C)(C(F)(F)(F))(C(F)(F)(F))Oc(=O)Occc
11/C3F6HCO3Cctc-B3LYP-6631xGss.out	-0.30199	-0.0261	-8.22	-0.71	C(C(F)(F)(F))(C(F)(F)(F))Oc(=O)OCc#c
COc(=O)OCCC (MePrCO3)					





- Organic synthesis/electrochemical testing/surface characterization/organic re-synthesis (Xu, Cresce, Russell)

From Computer to Glassware…

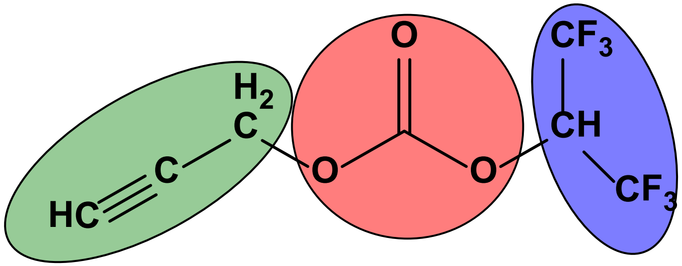
Key sub-structures synthetically integrated into a single molecule

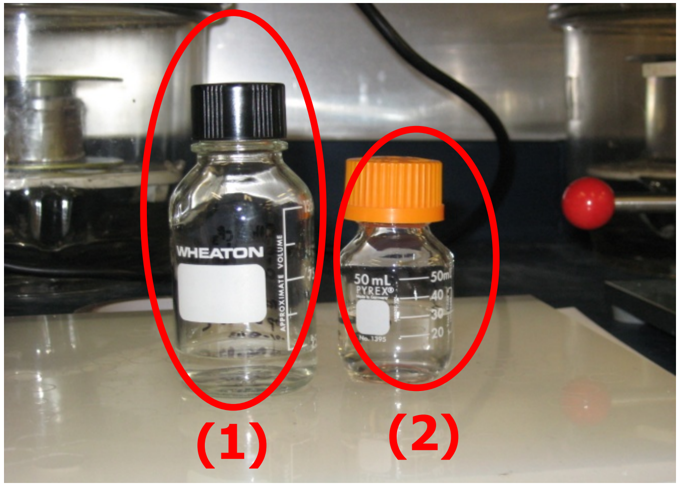
Synthesis of the new concept compounds:

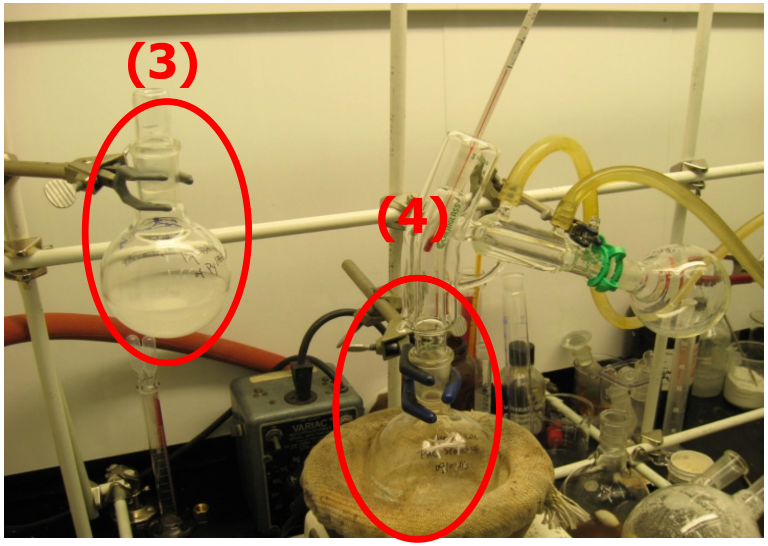
- 9 successes, >15 failures

All new compounds

- No hits in SciFinder
  - New molecules never existed before
  - Patent in process
- Complete ARL IP
- Ready for scale-up at ANL MERF

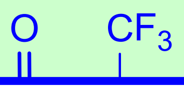
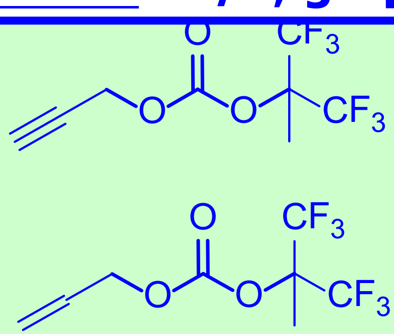
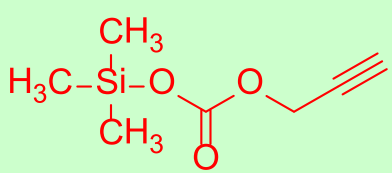
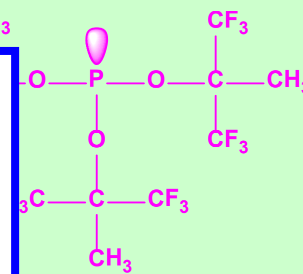






Summary of New Additives Made in FY2014

Multi-functional Units integrated into a Single Molecule

Functional Carbonates	Functional Silanes	Phosphite
  * structure and purity both confirmed	   * structural confirmation on-going	 * purity still an issue to resolve

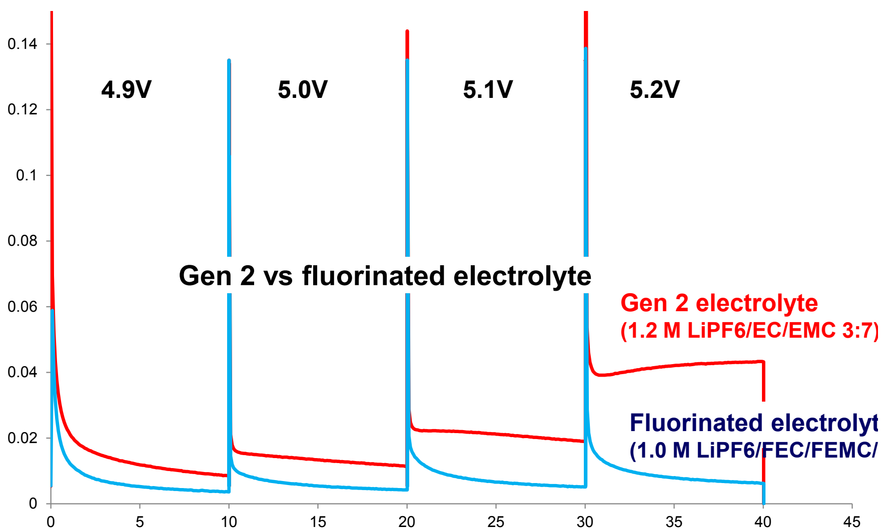
Electrochemical characterization on-going in FY 15

Cycling, floating test, etc:

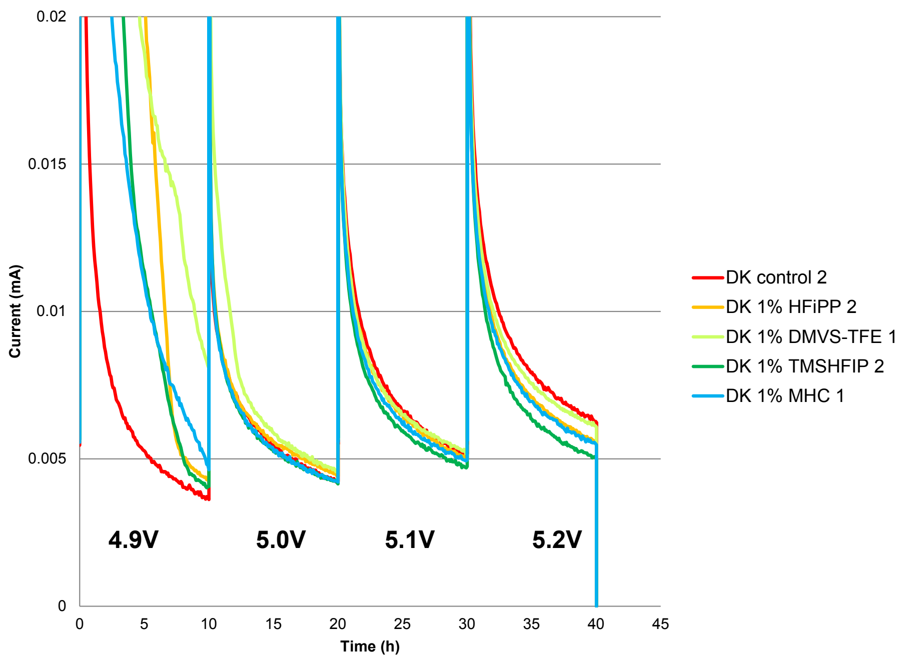
- **<u>cathode</u>: high V LMNO, S/C composite…**
- **<u>anode</u>: Si/C, graphite**

Preliminary Characterization

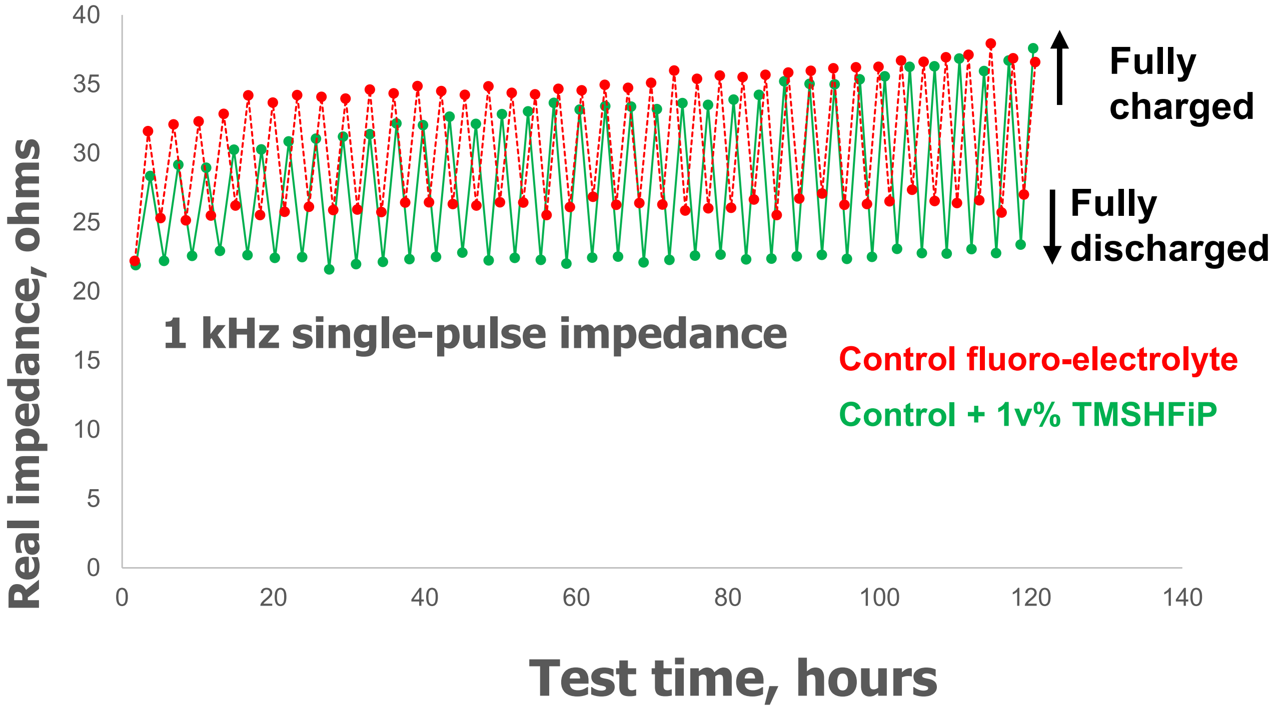
Two baseline electrolytes selected as baseline
- Aggressive floating tests were performed as rapid screening tool
  - full Li-ion cells after initial cycling/forming
- Advantage of fluorinated electrolyte against oxidation is apparent



- Effect of additives on Fluorinated Baseline
  - Similar but smaller effects as compared with Gen 2



Effect of TMSHFiP on Impedance



Fluoro-electrolyte with 1 vol% TMSHFiP additive cycles with lower impedance in both charged and discharged states.

Conclusions

1. TMSHFiP silane effective in Gen 2 carbonate and fluorinated electrolyte system.
   - Significantly reduces charge consumed by oxidation of Gen 2 carbonates
   - Observed decreased 1 kHz cycling impedance in fluorinated electrolyte
2. None of the propargyl-containing additives works
   - Too reactive for any electrolyte/LNMO combination
   - Stable radical may form shuttling species
   - DMVS-TFE very promising for Gen 2 carbonate system

TMSHFiP additive: a descendant of the HFiPP phosphate-based electrolyte additive;
MHC: a fluorinated carbonate

Collaboration and Coordination with Other Institutions

Collaboration:

- ✓ **U.S. Army Research Laboratory (Dr. Kang Xu, Project team member)**
- ✓ **Brookhaven National Laboratory (Dr. Xiao-Qing Yang, Project team member)**
- ✓ **University of Texas - Austin (Prof. Arumugam Manthiram)**
- ✓ **Center of Nano-Materials, Argonne National Laboratory (Dr. Larry Curtiss)**

Interactions:

- University of Rhode Island (Prof. Brett Lucht)
- Jet Propulsion Laboratory (Dr. Marshall Smart)
- Lawrence Berkeley National Laboratory (Dr. Vincent Battaglia)
- Cell Analysis, Modeling, and Prototyping Facility (CAMP) (Dr. Andrew Jansen)
- Material Engineering and Research Facility (MERF) (Dr. Gregory Krumdick)
- Arkema (Dr. Ryan Dirkx)
- NEI (Dr. Ganesh Skandan, Dr. Nader Hagh)

Summary

- Argonne took a combined approach to tackle the voltage instability of electrolyte by developing the fluorinated carbonate-based electrolytes with intrinsic stability and the passivating cathode additive to afford a stable electrode/electrolyte interphase.
- An effective probing tool was established for electrolyte oxidation stability by electrochemical floating test.
- Fluorinated cyclic carbonates and fluorinated linear carbonates were synthesized and characterized and their electrochemical performance were evaluated in LNMO/graphite cells.
- FEC and TF-PC based electrolyte have achieved superior capacity retention especially at elevated temperatures in 5-V LNMO/graphite cells. Post-test analysis showed that the fluorinated electrolytes are much more stable in both the liquid electrolyte phase and on the electrolyte/cathode interface.
- Lithium compensation provides an efficient way to further improve the LNMO/graphite cells with a more stable fluorinated electrolytes.
- LNMO/graphite cells with fluorinated electrolytes showed improved self-discharge at elevated temperature at fully charged state.
- New electrolyte additives were synthesized and characterized; Live-formation of SEI by F-solvent was observed by *in-situ* electrochemical AFM.
- New fluorinated sulfone-based electrolyte is in process.

Proposed Future Work

For the rest of the FY15, we will continue to explore the fluorinated carbonate-based electrolytes to enable the high voltage high energy cells.

- ✓ Synthesis and development of new additives tailored to stabilize the thermally stable fluorinated electrolyte TF-PC3.
- ✓ Investigate the Li^+ solvation in the fluorinated electrolytes by 2D-DOSY NMR.
- ✓ Electrode surface analysis using XPS and HR-TEM.
- ✓ Scientific write-up for publication in peer-reviewed journals.

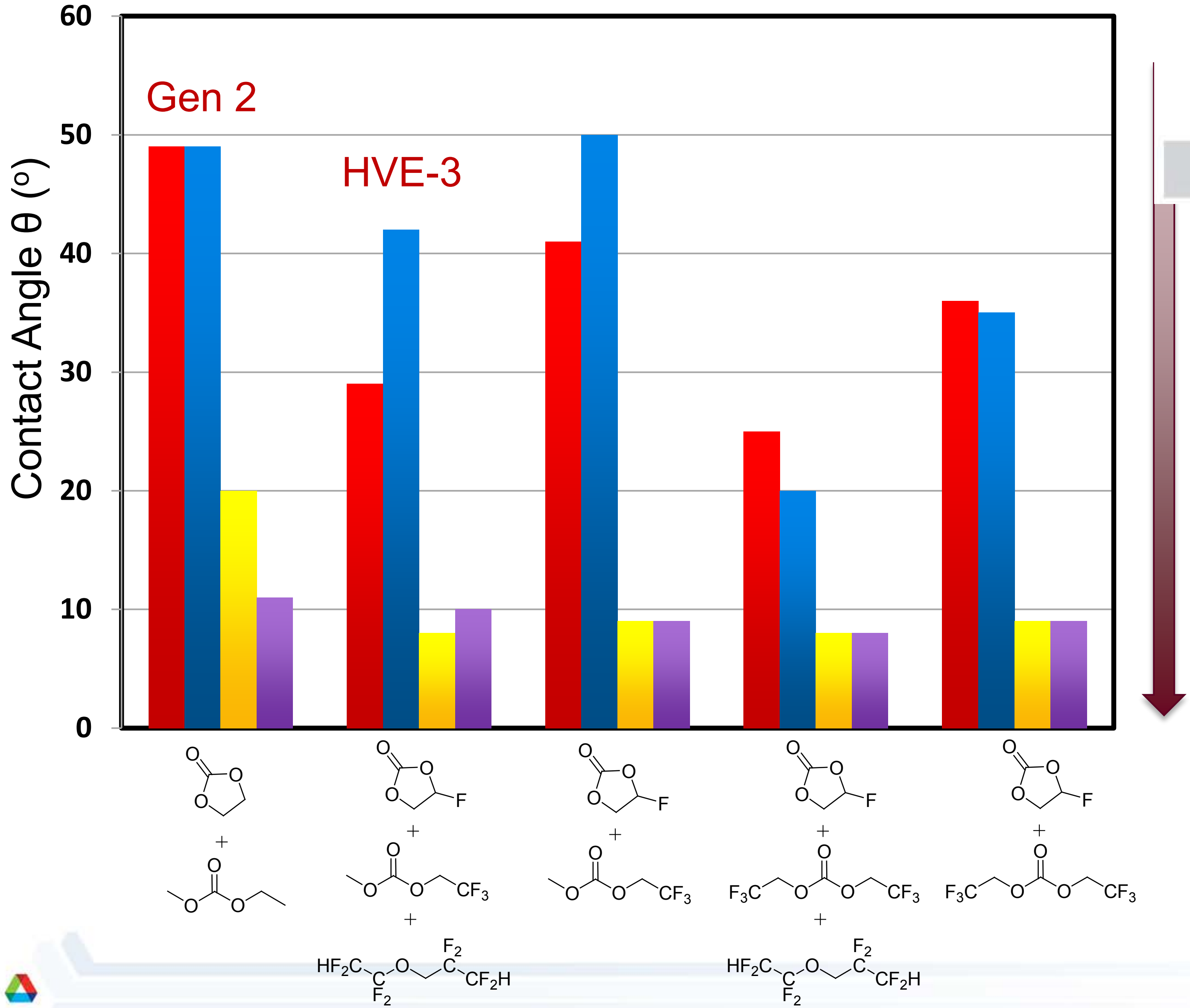
For the rest of the FY15, we will initiate the fluorinated sulfone-based electrolyte study for high voltage high energy Li-ion cells.

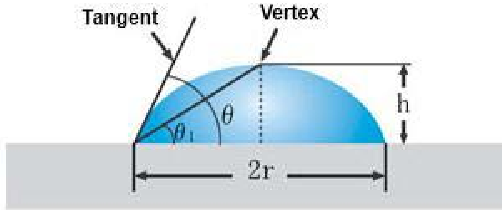
- ✓ DFT modeling of the electrochemical window of fluorinated sulfone.
- ✓ Synthesis and characterization of new fluorinated sulfone solvents.
- ✓ Evaluation of electrochemical performance.

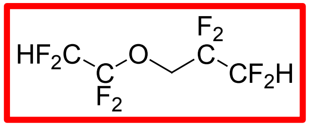
Technical Back-Up Slides

Other Benefits of Fluorinated Electrolytes

Improved wetting (contact angle measurement)

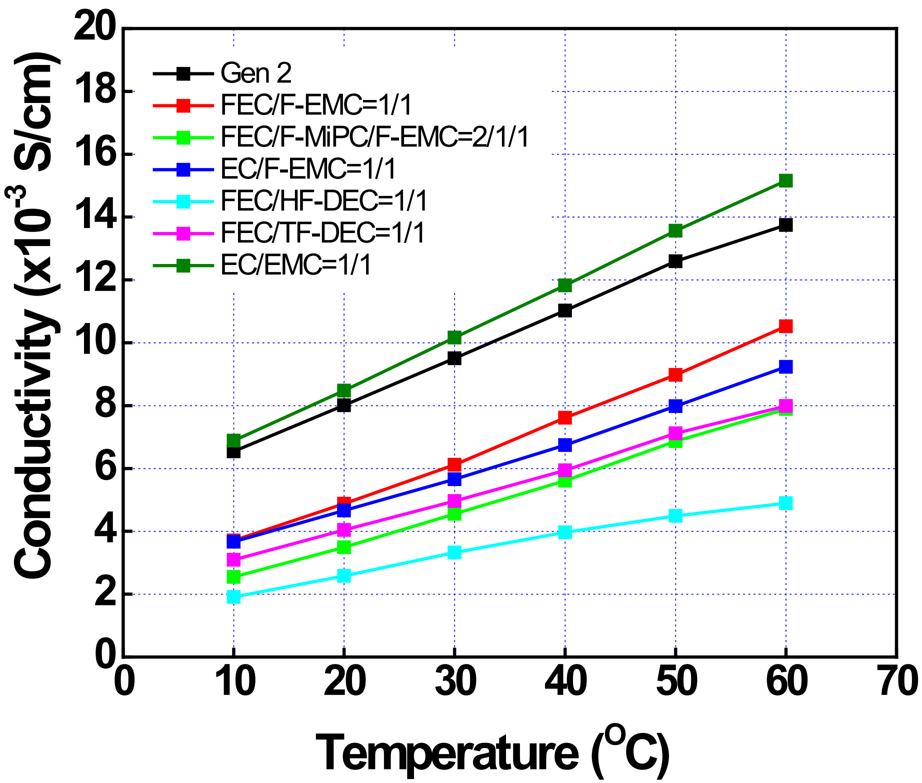


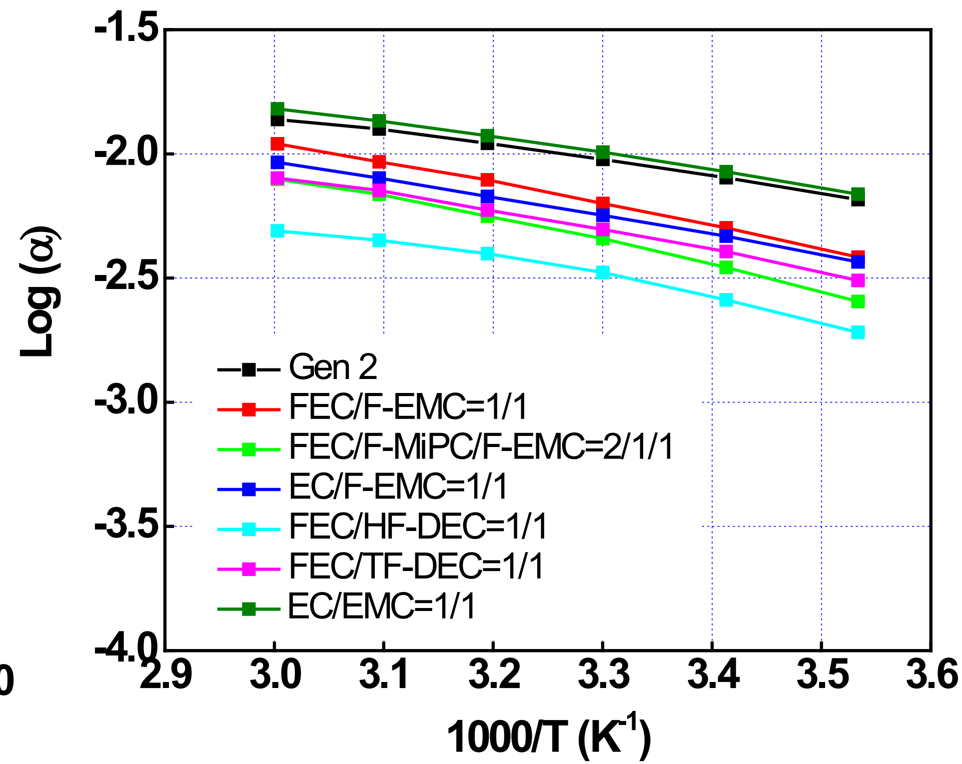




Improves wetting!

Conductivity for New Linear Carbonate formulations





Conductivity: